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# A Study to evaluate the permeation characteristics of black tea flavors and linalool in four different plastic films

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**A STUDY TO EVALUATE THE PERMEATION CHARACTERISTICS  
OF BLACK TEA FLAVORS AND LINALOOL  
IN FOUR DIFFERENT PLASTIC FILMS**

**By**

**Samuel Aw Cheong Soon**

**A THESIS**

**Submitted to the**

**Department of Packaging Science**

**College of Applied Science and Technology**

**in partial fulfillment of the requirements**

**for the degree of**

**MASTER OF SCIENCE**

**Rochester Institute of Technology**

**1995**

College Of Applied Science And Technology

Rochester Institute Of Technology

Rochester, New York

## CERTIFICATE OF APPROVAL

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### M.S. DEGREE THESIS

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The M.S. Degree Thesis of Samuel Aw Cheong Soon

Has Been Examined And Approved By

The Thesis Committee As Satisfactory

For The Thesis Requirements For The

Master of Science Degree

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Date 15 Nov 1995

## Title of Thesis

A Study To Evaluate The Permeation Characteristics Of Black Tea Flavors  
And Linalool In Four Different Plastic Films

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## **ABSTRACT**

The use of plastic films has seen tremendous growth during the past decades. The US Flexible Packaging Association 1994 Annual Report revealed that flexible packaging sales are predicted at US \$13.2 billion and 50% of the flexible packaging is produced for food items. It is also realized that polymeric films interact with their environments differently than do glass or metal containers. Volatile flavor compounds from food items can dissolve and diffuse in the polymeric membrane. These movement is especially important when the loss of these flavors results in the lowering of the product quality and acceptance.

The permeation characteristics of black tea flavors and linalool were evaluated in four different plastic films (QHE, MET-HB, AOH and Barex), using an isostatic test procedure. Presently there is no data available for black tea flavors and only very little data for linalool, on the transport of such organic penetrants through plastic membranes. The permeation results collected from the MAS 2000, Organic Flavor Detector, suggested that each film has a different barrier property to linalool and the black tea flavors. The relationship between the permeation characteristics of linalool and the black tea flavors could not be established at this present time, as more data are needed to verify the permeation profile in each film, especially for the black tea flavors. Recommendations for further improvement and research were suggested to determine which of the four films would offer the best flavor barrier to linalool and black tea at room temperature.

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## I. INTRODUCTION

The shift from absolute barrier type packages such as metal cans and glass bottles, to semi-permeable polymeric packaging systems, has created a need to develop better understanding of the transport of gases and vapors through polymer films. The transport of permeants such as oxygen, carbon dioxide and water vapor through polymer structures has been the subject of numerous investigations. Standard test methods and procedures are available for determining transmission rates for these permeants (ASTM E96-66, ASTM D3985-81). In contrast, although the transport of organic penetrants through packaging materials has been the subject of several recent investigations, there is a scarcity of data available in this area. Knowledge of the diffusion, solubility and permeability of organic penetrants through polymer structures is both of theoretical and practical importance. In terms of theoretical importance, such studies can aid in developing a better understanding of the mechanism of diffusion of organic penetrants through polymer membranes and particularly for the case of permeant molecules that have strong interaction with the polymer. The diffusion and solubility of organic penetrants will be of practical importance for cases when product quality is related to the transfer of organic vapors from one element of the package to another. For example, the aroma barrier properties of a package system are important, since the retention of product aroma constituents and the exclusion of sensorially objectionable organic molecules from the

package external environment contribute to the keeping quality and thus, the shelf life of the product. Further, knowledge of the aroma barrier properties of polymeric packaging materials can provide a means of designing and/or selecting a barrier structure for a specific end use application. Knowing solubility data for essential flavor ingredients in certain polymers is of paramount importance in avoiding the effect of ‘flavor scalping’<sup>1</sup>. Since the flavor compounds are normally present in low concentration in the foodstuff, such as tea leaves, there is a tendency to ‘lose’ the aroma constituent due to absorption by the package film.

In summary, this study seeks to determine the diffusion coefficient(D), solubility coefficient(S) and permeability coefficient(P), to accurately describe the mass transfer behavior of penetrant/barrier systems involving organic vapors. This is important to predict the changes in the quality of packaged black tea that are related to loss of aroma during storage. Black tea has approximately 600 flavor components. Studying the permeation characteristics of each flavor permeant is beyond the scope of this research. Hence, only linalool, which is one of the major flavor compound in black tea, and all the flavor components as a group, are studied.

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<sup>1</sup> Ruben J. Hernandez, Journal of Plastic Film & Sheeting 1986 p 187-190.

## **II. THE PROBLEM AND ITS SETTING**

### **A. Statement of the Problem**

The permeation characteristics of black tea flavors and linalool was evaluated in four different plastic films (QHE, MET-HB, AOH and Barex).

### **B. The Subproblems**

#### **1. Subproblem 1**

The first problem is to detect the very minute and volatile flavor components present in black tea and linalool permeating through the plastic films. A highly sophisticated instrument with extremely high sensitivity and accuracy is required.

#### **2. Subproblem 2**

The second problem is to establish if there is a relationship between the permeation characteristics of black tea (which contains more than 600 flavor components) and linalool (an organic flavor component present in black tea) in the four plastic films.

## **II. C. Hypotheses**

### **1. Hypothesis 1**

There is no difference in the barrier properties of the different films to linalool found in black tea leaves.

### **2. Hypothesis 2**

The second hypothesis is that there is no relationship in the permeation characteristics of the black tea flavor components and linalool in the four plastic films.

## **D. Delimitations**

This study would only look into the permeation characteristics of one black tea sample, the Lipton Yellow Label Tea, CTC (an automatic process in which the tea leaves undergo Cutting, Tearing and Curling simultaneously), Extra Strong Extra Flavor, manufactured and packed by Lipton India, Limited. This is because other teas may have different organic flavor profiles and thus would yield different permeation characteristics.

The films used for this research are:

1. Acrylonitrile film (Barex) from BP Chemicals,
2. Coextruded unmetallised oriented polypropylene film (QHE) from an anonymous film supplier X
3. A metallised oriented polypropylene film (MET-HB) and
4. A multi-layered bi-axially oriented polypropylene film (AOH) from an anonymous film supplier Y.

The study will be confined to these four types of films submitted by these three suppliers. Other films from the same basic plastic materials, namely polypropylene and acrylonitrile, may yield different permeation results as the films may be manufactured differently by different suppliers.

## **E. Definitions of Terms**

### **1. Membrane**

The barrier through which some gases or organic flavors is migrating is called a membrane. In this case, it shall be the four plastic (polypropylene and acrylonitrile) films submitted by the three suppliers.

## II. E. 2. Permeant

The substance migrating through a membrane is called a permeant.

In this case, it shall be the organic flavor components in the black tea and linalool.

### 3. Permeation Characteristics

Permeation occurs in three stages. When a permeant migrates through a membrane, it first dissolves in the membrane. After which, it diffuses through the membrane and finally evaporates out of the membrane.

#### a. Permeability

The permeability coefficient (P) of a permeant in a membrane is directly proportional to the solubility coefficient (S) and the diffusion coefficient (D) in the membrane under steady state condition. {  $P = D \times S$  }

#### b. Solubility

The solubility measurement describes the degree to which the membrane will retain or absorb the permeant.



**II. E. 3. c. Diffusion**

The rate at which the permeant will migrate through the membrane.

**4. Linalool**

Linalool, an important and relatively abundant organic constituent of black tea flavors. It gives a leafy and floral aroma.

**II. F. Assumptions**

1. The first assumption is that black tea volatile flavor components and linalool will permeate through the different plastic membranes.
2. The second assumption is that these different permeation rates can be identified by mechanical test and/or sensory evaluation test.
3. The third assumption is that if there is a relationship between the permeation characteristics of the black tea flavor components and linalool, it can then be used as a reference or guide to predict the permeation characteristics of Lipton Yellow Label Tea and other flavory black tea which contain large amount of linalool.

## CHAPTER 1 BACKGROUND TO RESEARCH

### I. Tea Flavors & Its Quality

The flavor of a foodstuff is an integrated response composed primarily of the sensations of aroma and taste. Although color and texture may also modify the overall product's flavor assessment, the odor or aroma is the single most important contributor to the characteristic flavor of most foods<sup>1</sup>. Flavor testing is a common appraisal step in the buying and selling of tea. Tea classification is done initially in the country of origin or manufacture, where the lots of tea are first classified, by appearance, into types: then these rough gradings are further classified, by smell and/or taste, and finally into price grades within the types. On the arrival of the tea at the country of destination, the dry tea is again inspected for color, size uniformity, smell and even taste, before any repacking operations can be undertaken. Tea flavor is unique among various beverages and an important factor in determining tea quality. Hence, preserving the volatile flavor components of the tea leaves, throughout the product distribution cycle, is of paramount importance to maintaining product quality and sales. The chemical nature of the tea flavor constituents, the mechanisms of flavor formation during tea leaf processing, and the objective estimation of finished tea flavors, are all subjects that have been the focus of interest of many researchers. However, our knowledge of tea flavors, is

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<sup>1</sup> Denis A. Cronin, Food Flavors Part A. Introduction 1982 p 15

still inferior to that of our understanding of the constituents of tea taste and color<sup>2</sup>.

The interactions of volatile food flavors with packaging materials, is a totally new area that food scientists are studying today. The use of high barrier plastic films to minimize or eliminate flavor loss is the focus of much research today.

## **II. Black Tea Flavors**

The appealing characteristics of black tea as a beverage are its taste, aroma and color. The essential oil in fresh tea leaves and volatile compounds developed during the manufacturing process form the characteristics tea flavor<sup>3</sup>. Several studies have reported various compositions of the volatile flavor compounds (VFC) or aroma complex, and over 600 individual components have been reported.<sup>4</sup> However, which of the black tea aroma constituents and in what amount, are really essential in determining the character of this beverage is still unknown<sup>5</sup>. Many scientists believe that the aroma of tea is based on the proportion of a number of key compounds. In Sanderson's review<sup>6</sup>, he postulated the possibility of an as yet unidentified aroma constituent as the primary determinant of the character of black tea aroma. This is yet to be ruled out or confirmed. Further development of different isolation, fractionation and separation

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<sup>2</sup> Mikhail A. Bokuchava, Food Flavors Part B. The Flavor of Beverages 1986 p 49

<sup>3</sup> Yamanishi T. Handbook of Food & Beverage Stability 1986, chap 12.

<sup>4</sup> Robinson J. M. Tea: Cultivation To Consumption 1991, p 603-647.

<sup>5</sup> Walter Mick. J. Agric. Food Chem. 1984, 32: 924-929.

<sup>6</sup> Sanderson , G., Black Tea Aroma & Formation 1975 p 65-97.

techniques, and better analytical instruments such as nuclear magnetic resonance, infrared and mass spectrometry, may lead to more discovery of new components in tea volatiles, though it seems that most of the volatile aroma components have been determined.

### III. Linalool

After much research into black tea of different origin, Yamanishi et al. inferred that the best quality black tea contains large quantity of linalool and linalool oxides and smaller quantities of geraniol and 2-phenylethanol.<sup>7</sup> Gianturco et al. also reported that linalool is of particular importance for black tea aroma after determining the quality of black tea by computerized analysis of aromagrams.<sup>8</sup> Hence, for this research, linalool is selected as the reference permeant in this study.

Linalool has a molecular formula of  $C_{10}H_{18}O$  and was discovered in 1937. It is found in black tea and is considered to be an important contributor to its flavor. Besides, linalool is also found in fresh tea leaves, green tea and oolong tea (semi-fermented). Linalool is a monoterpene, that is, a  $C_{10}$  compound that has been constructed from isopentene units. Linalool also exists in its oxides form. Linalool oxide has a chemical formula of  $C_{10}H_{18}O_2$ .

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<sup>7</sup> Yamanishi et al. J. Agri. Biol. Chem. 1968, 32: 370-386.

<sup>8</sup> Gianturco et al. J. Agri. Food Chem. 1974, 22: 758-761.

#### IV. Tea Flavors & Storage

Teas are often subject to varying periods of 3-6 months of storage from the time of production to reaching consumers. The changes that occur during storage have been studied by several researchers, who have identified factors which affect the characteristics of tea. Among these are the increase of moisture accompanied by the growth of micro-organisms<sup>9</sup>, increase in thearubigins and extractable caffeine, and decline in theaflavin levels.<sup>10</sup> An important factor in the decline of theaflavin levels in black tea is the residual polyphenol oxidase and peroxidase activity, which are still present even after processing. It was also shown that storage of tea under extreme conditions of low temperature, low moisture, and low oxygen availability, lead to a significant reduction of enzymatic activity and decreased the deterioration rate of theaflavin during storage.

Studies of chemical changes occurring during storage also showed that **storage led to a loss of flavor** and astringency, and the development of undesirable characteristics.<sup>11</sup> These changes were accompanied by lipid hydrolysis; loss of theaflavins, amino acids, sugar and photosynthetic pigments. All these were accelerated by high moisture and elevated temperatures. Specific investigations into black tea during storage revealed the following: there was a reduction in vitamin c content, change of color from bright brownish black to dull brownish or

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<sup>9</sup> R. L. Wickremasinghe Tea Q., 1972, 43 p 147.

<sup>10</sup> J. B. Cloughley J. Sci. Food Agric., 1981, 32 p 1213-1229.

<sup>11</sup> G. V. Stagg J. Sci. Food Agric., 1974, 25 p 1015.

grayish brown, change in aroma from leafy and refreshing to dull and heavy, change of well balanced taste of astringency and bitterness to 'flat' taste. These changes were accelerated by moisture, oxygen, elevated temperatures and exposure to light.<sup>12</sup> The sensory quality of briskness, strength and flavor all declined during storage and all contributed to the loss of value. Therefore, the basic understanding of the factors which bring about these undesirable changes during the storage of tea is needful for the design and development of a suitable package system: to preserve the quality of black tea more effectively and efficiently. This will inevitably help prevent flavor deterioration but will also stabilize the market prices of tea.

## **V. Tea Flavors & Packaging**

Most tea is shipped in bulk and then repackaged in the tea consuming countries, such as England. For instance, almost the entire quantity of tea produced in India is packed in traditional 12-batten plywood chests which are inner-lined with aluminum foil juxtaposed with tissue paper. A standard plywood chest of size 40 X 50 X 60 cm holds, on an average, 50 kg of tea. Loose tea for retail sale is packaged in a multitude of different shapes, sizes and types of materials, the most common being a paperboard carton with either an aluminum foil liner or an overwrap of PP. Metal containers with snap-on lids are also used for some

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<sup>12</sup> T. Yamanishi Handbook of Food & Beverage Stability 1986 p 665.

premium products. Tea bags have also become the most popular form of retail packaging and considerable development has gone into improving the tissue paper used for this type of package, porous wet-strength paper being required. Once filled, the tea bags must be placed inside a package which provides an adequate barrier to moisture vapor. Paperboard cartons overwrapped with PP are most common. Much research and development of new alternative packaging materials for the bulk shipping of black tea is currently being conducted -- in view of the increasing shortage and the rising cost of conventional packaging materials (plywood chest lined with aluminum foil-tissue paper). The problem of disposal of the empty tea chest, as encountered in importing countries like the UK and USA<sup>13</sup> must also be addressed. Besides, changes in consumer behavior, have also caused companies and manufacturers to look into the package design more seriously, to meet the needs of the retailers and the modern end-users.

## **VI. Tea Flavors & Consumers**

As the consumers gained more knowledge and became more sophisticated about the quality of tea, its flavor becomes a very important issue. No longer are consumers simply looking for good color and taste in tea, but also its scent or smell. Hence, packaging becomes an integral and crucial aspect of marketing. The package has to keep the aromatic tea volatile flavor components in and exclude

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<sup>13</sup> S.N. Stephen Thanaraj Recent Developments in Packaging of Black Tea, UPASI.

other taints out. The packaging must preserve all the desirable tea attributes, while on the shelf, and at the same time, promote sales.

**Table 1: Consumption of Tea in Various Countries, 1987 -1989**

**(International Tea Committee, Annual Bulletin of Statistics, London 1991)**

<b>Country</b>	<b>Total (metric tons)</b>	<b>Per capita (kg)</b>
Australia	18.56	1.12
Canada	14.15	0.55
Hong Kong	9.60	1.69
India	462.00	0.58
Japan	117.72	0.96
Kenya	17.53	0.73
New Zealand	5.24	1.59
Sri Lankan	21.00	1.27
United Kingdom	160.99	2.81
USA	84.20	0.34



Table 1 shows the consumption of tea in various countries. By analyzing the per capita consumption for each country, the USA has the lowest number. This indicates that the US market is not as big as others, and the reason maybe due to its package design. The usual pack of tea in US is commonly packaged in paperboard with a PP overwrap or sometimes in a wax-coated paper bag which is then placed into a paperboard carton. All these packaging materials used are not sufficient to provide the necessary barrier during storage. As the turnover of the product is rather slow, the quality deteriorates with time. Hence, the author's major Professor Fritz Yambrach, suspects that the US population has not been properly being exposed to real, fresh quality tea.

In retrospect, having visited UK in August 1995, the author found that the packaging materials for tea are rather similar to the US, except for the brands and the graphics displayed. However, because the consumption of tea is much higher in Britain, the barrier property of the package, in this case, is not as crucial as that, being required in the US, for the product is consumed fairly quickly and the time spent in distribution is short. . Another interesting observation is that the tea bag sizes in UK vary from 1.5 g for the economy products up to 3.15 g. Many teas currently sold in Canada and the USA, however, need to contain as much as 3.50 g of tea in the tea bag. If good barrier package is used, the amount of tea needed to give sufficient quality flavor can be reduced significantly.

Hence, to expand the US market, improved tea flavor quality by improvement in package is a key to success. Some newer packages being examined in tea packaging include using 30  $\mu\text{m}$  metallised polypropylene pouches, vacuum pack, using 12/50  $\mu\text{m}$  metallised polyester laminated to polyethylene pouches and nitrogen flushed (oxygen < 1.0%), using 12/50  $\mu\text{m}$  metallised polyester laminated to polyethylene pouches. More developmental work is in progress to find the most effective and economical package for tea, to satisfy the needs of the consumer.

## CHAPTER 2 REVIEW OF BLACK TEA

### I. History of Tea

Chinese mythology teaches that in 2737 B.C., tea was a drink sent from heaven to the Emperor Shen Nung. One fine day, the Emperor was out on an outing to the country-side. While his courtiers were preparing his afternoon meal, a puff of wind blew tea leaves into a pot of boiling water. As the Emperor watched, the tea transformed the water into a beverage of great joy and pleasure for him. Since then, tea has become deeply entwined with the Chinese's, as well as the Asian's, culture and history. Its greatest boost in popularity came after it was added to the Buddhist religious ceremony. As Buddhism spread into new regions, new locale was also scouted for its growth. Today, tea is grown in India, China, Sri Lanka, the former Russia, Japan, Indonesia, Africa, Turkey, Bangladesh, Malawi, South America, Australia, Malaysia, Korea and many other parts of the world.

It was recorded that in the early Roman Empire, caravans carried gold to the East would return with silks, spices and tea. The first account of tea reached the Arabs in AD 850; the Venetians in 1559; the English in 1598; the Portuguese in 1600. It reaches Russia in 1618; Paris in 1648 and America in about 1650. Ironically, when tea was first brought to Britain, coffee was the beverage of choice. An attempt to protect the coffee industry had led to a series of import taxes on tea. American

colonists, all dedicated tea drinkers, bridled at this English taxation and used the Boston Tea Party as a rallying cry for the Revolutionary War.

Today, tea remains an essential part of everyday life throughout Asia and Europe. But in the U.S., tea has typically taken a back seat to coffee and soda as the beverage of choice. However, this seems to be changing now as tea companies are winning consumers who seem to have just "discovered" this ancient beverage. More than 140 iced tea offerings are now on US store shelves as Coke, Pepsi and Snapple war for the Number 1 spot in the increasing crowded ready-to-drink iced tea arena. Beverage manufacturers are not content to limit their tea exploits to iced teas but several such as Snapple and Gatorade, are using tea as a flavoring in other beverages. Whether blended with other flavors or sold straight and clear, tea seems to have secured a definite place in the beverage industry.

## **II. Introduction : World Production**

The tea plant, *Camellia sinensis*, is a very important agricultural and commercial product with a unique horticulture and manufacturing process. Tea beverages are prepared from the leaves of *Camellia sinensis*. Second only to water, tea is the most widely consumed beverage in the world today with an annual per capita consumption exceeding 40 litres (Annual Bulletin of Statistics 1990, London).

The principal tea-growing area are China (the first country in which tea was grown and where more varieties of tea are produced than in any country), India (which produces about one third of the world's tea and exports to 80 different countries), Sri Lanka (also known as Ceylon tea), East Africa (chiefly Kenya, Uganda, Rwanda, Burundi, Tanzania, Malawi and Zimbabwe), Mauritius, Papua New Guinea, Japan, the former Soviet Union, Turkey, Bangladesh, Taiwan, Indonesia, Iran and parts of South America.

**Table 2 1990 World Tea Production in Million Metric Tons (Annual Bulletin Statistics of 1990, London)**

<b>Geographic Region</b>	<b>Black Tea</b>	<b>Green Tea</b>	<b>Total Tea</b>
<b>Asia</b>	<b>1.530</b>	<b>0.471</b>	<b>2.001</b>
<b>Africa</b>	<b>0.323</b>	<b>0.000</b>	<b>0.323</b>
<b>South America</b>	<b>0.039</b>	<b>0.000</b>	<b>0.039</b>
<b>Oceanic</b>	<b>0.009</b>	<b>0.000</b>	<b>0.009</b>
<b>USSR</b>	<b>0.092</b>	<b>0.023</b>	<b>0.115</b>
<b>Total</b>	<b>2.003</b>	<b>0.494</b>	<b>2.497</b>

### **III. Botany & Agriculture**

The tea plant is indigenous to China and South East Asia. It has been classified as *Camellia sinensis* and has two common varieties, *sinensis* and *assamica*. The variety *sinensis* is a shrub-like plant growing to a height of 4 to 6 meters with leaves 5 to 12 centimetres long. This variety is more commonly used in agriculture. The variety *assamica* grows to 12 to 15 meters in height and has leaves of 15 to 20 centimetres in length.

Geographical areas having an annual rainfall of 50 inches or more per year and an average temperature of 86 degrees F are most favourable for tea growth (Graham H, 1983). Traditionally, *Camellia sinensis* has been propagated, hybridised and bred through seeds. To maintain genetic purity and more rapidly establish new productive stands of tea, vegetative propagation are practised commonly now. Leaf cuttings are taken and planted in nurseries where they develop into seedlings within 24 weeks. These seedlings are transplanted to the fields and new stands of tea are ready for harvesting in 3 years.

In the fields, tea is maintained as a shrub-like bush through frequent harvesting. The emerging shoots and young leaves of the plant, called the flush, are harvested every 8 to 12 days. The flush is rich in polyphenols and enzymes which are important compounds in tea manufacture and its subsequent quality. Harvesting can be done manually. However, mechanical harvesting is carried out in areas

where labour is expensive and where the tea is grown in steep mountain slope. Immediately after harvest, the tea leaves are transported to the tea factories for manufacturing. It is the manufacturing process that determine the type of tea to be produced. There are three general types of tea produced: black tea (fully fermented), green tea (unfermented) and oolong (partially fermented).

#### **IV. Black Tea Production**

The leaves are withered in trays or drying racks in drying rooms, or are drum dried; this involves dehydration, reducing the moisture content of the fresh leaves from about 75% to about 55-65% so that the leaves become flaccid, a prerequisite for the next stage of processing; rolling without cracking of the leaves. Withering at 20-35 degrees C last about 4-18 hours. During this time the thinly spread leaves lose about 50% of their weight in air or in a stream of warm air as in drum drying. In the next stage of processing, the leaves are fed into rollers and are lightly, and without pressure, conditioned in order to attain a uniform distribution of phenoloxidase enzymes which are present in the epidermis tissue cells. This is followed by a true rolling step in which the tea leaf tissue is completely macerated by conventional crank rollers under pressure. The cell sap is released and subjected to oxidation by oxygen from the air.

The rolling process is regarded as the first stage of fermentation which proceeds at 35-40 degrees C for 45 min to 4 hours for tea leaves spread thinly in layers 5-7.5 centimetres thick. The fermentation is stopped when the leaves attain the bright, coppery-red colour of a minted copper coin and an odour resembling that of sour apples. Then the fermented tea leaves are heated in large ovens or firing machines or desiccators at 87-93 degrees C for 20-22 minutes, or more recently, by a fully automated process. The firing reduces the moisture content to about 3%, the tea aroma is fixed, and the coppery-red colour is changed to black, hence termed as black tea. Black tea accounts for over 90% of all tea consumed by Americans and over 85% of all tea consumed by the world.

In the factories of India and Sri Lanka, rollers and machines in continuous operation are used - the so-called CTC machines (cutting, tearing and curling) provide simultaneous crushing, grinding and rolling of the tea leaf, thus reducing the rolling and fermentation time to 1 to 2 hours.

## **V. Grades of Tea**

The numerous grades of tea found in the trade are defined by origin, climate, age, processing method and leaf grade. They can be generally classified into:



**A. Leaf Grade**

Tea with full intact leaves, such as Flowery Orange Pekoe and Orange Pekoe made from leaf buds and the youngest, hairy, silver leaves with yellowish tips; Pekoe (the third leaf); Pekoe Souchong with the coarsest leaves, fourth to sixth, on the young twig.

**B. Broken Leaves**

Broken-tea, with broken or cut leaves similar to the above grades, in which the fine broken or cut teas with the outermost golden leaf tips are distinguished from the coarse, broken leaves. Broken or cut (loose tea) is the preferred product in the world trade since it provides a finer aroma which, because of increased surface area, produces larger amounts of the beverage.

**C. Fannings**

Fannings and the fluff from broken or cut leaves, freed from stalks or stems, are used preferentially for manufacturing of tea bags.

**D. Tea Dust**

Tea dust, which is the fines collected during the sifting of the tea leaves after the firing or final drying operation. It is not used in Europe.

### **E. Brick Tea**

It is made of tea dust by sifting, steaming and pressing the dust together with the aid of a binder into a stiff, compact tea-brick. This is not available in the European market.

All over the world, there is blending of teas,(examples Chinese, Russian, East-Friesen blends, household blends) to adjust the quality and flavor of the brewed tea to suit consumer taste, acceptance or trends and to accommodate regional cultural practices for tea-water ratios. Like coffee, tea extracts are also dried and marketed in the form of a soluble powder, often called instant tea.

## **VI. Common Varieties of Black Tea Found In The Market**

### **A. Assam**

A fine, malty black tea with a rich, robust flavor from Assam, India, one of the world's major producing areas. The best quality Assam have golden tips.

### **B. English Breakfast**

A strong flavored blend, often of both Indian and Sri Lankan black tea.

**C. Sri Lanka**

High grown Sri Lankan tea has a rich, brown colour and brisk, pungent taste with a lemony aroma, making it suitable for drinking at any time of the day.

**D. Darjeeling**

Grown in the foothills of the Himalayas, Darjeeling has a distinct muscatel flavor coupled with an exquisite aroma. Darjeeling, especially if pure, can cost a bit more than most teas.

**E. Earl Grey**

It is a blend of China black tea that is scented and flavored with the oil of Bergamot, a pear-shaped citrus grown around the Mediterranean.

**F. Lapsang Souchong**

A smoked tea, from the Fukien Province in China with a unique flavor, pungent aroma and robust taste.

## **VI. Composition Of Tea**

The chemical composition of tea leaves varies greatly depending on their origin, age and the type of processing. In fermented teas, 38-41% of the dry matter is soluble in hot water; this is significantly more than for roasted coffee.

**Table 3 Composition of Fresh and Fermented Tea Leaves and of Tea Brew in Percent Dry Weight Basis (Source: H.D. Belitz Food Chemistry 1987: pg 695).**

Constituents	Fresh Flush	Black Tea	Black Tea Brew <sup>*</sup>
Phenolic compounds <sup>a</sup>	30.0	5.0	4.5
Oxidised phenolic compounds <sup>b</sup>	0.0	25.0	15.0
Protein	15.0	15.0	Trace
Amino acids	4.0	4.0	3.5
Caffeine	4.0	4.0	3.2
Crude fibre	26.0	26.0	0.0
Other carbohydrates	7.0	7.0	4.0
Lipids	7.0	7.0	Trace
Pigments <sup>c</sup>	2.0	2.0	Trace
Volatile compounds	0.01	0.01	0.01
Minerals	5.0	5.0	4.5

<sup>\*</sup> Brewing time 3 minutes

<sup>a</sup> Mostly flavanols

<sup>b</sup> Mostly thearubigins

<sup>c</sup> Chlorophyll and carotenoid

## **VII. A. Phenolic Compounds**

Phenolic compounds make up 25-35% of the dry matter of the content of the young, fresh tea leaves. Flavanol compounds are 80% of the phenols, while the remainder is leucoanthocyanins, phenolic acids, flavonols and flavones. During fermentation, the flavanols are oxidised enzymatically to compounds which are responsible for the colour and flavor of black tea. The reddish colour of the tea extract is largely due to theaflavins and thearubigins while the flavor intensity is correlated with the total content of phenolic compounds and polyphenol oxidase activity. The concentration of phenols decreases with time. Thus a good quality tea is obtained only from young leaves.

## **B. Proteins**

Enzymes such as proteinases break down the plant protein during withering, resulting in the rise of peptides and free amino acids. The observed oxidation of linolenic acid to cis-3-hexanal, which then isomerises to trans-2-hexanal, is catalysed by a lipoxygenase and a hydroperoxide lyase. Both aldehydes and their alcohols which are formed by enzymatic reduction contribute to the tea flavor.

## **VII. C. Amino Acids**

Free amino acids constitute about 1% of the dry matter of the tea leaf. Of this, 50% is theanine and the rest consists of other protein forming amino acids, example beta alanine.

## **D. Caffeine**

Caffeine constitutes 2.5-5.5% of the dry matter of the tea leaves. It is of importance for the taste of the tea.

## **E. Carbohydrates**

Glucose (0.72%), fructose, sucrose, arabinose and ribose are among the sugars present in the tea leaves. Rhamnose and galactose are bound to the glycosides. Polysaccharides found include cellulose, hemi-cellulose and pectic substances.

## **VII. F. Lipids**

Lipids are present only at low levels. The polar fraction (glycerophospholipids) in the young leaves is predominant while glycolipids predominate in the older leaves.

## **G. Pigments**

Chlorophyll is degraded during tea processing. Chlorophyllides and pheophorides (brownish in colour) are present in fermented leaves, both being converted to pheophytines (black) during the firing stage. Fourteen carotenoids have been identified in tea leaves. The main carotenoids are xanthophylls, neoxanthin, xiolaxanthin and beta carotene.

## **H. Volatile Compounds**

There are more than 600 volatiles being identified in black. It should be emphasised that aroma is greatly affected by the origin and the processing of the tea. Volatiles constitutes about 0.01-0.02% of tea dry matter. Intensive research to identify the most important constituents responsible for black tea aroma has been undertaken by many scientists all over the world.

## **VII. I. Minerals**

Tea contains about 5% minerals. The major element is potassium, which is half the total mineral content. Some varieties contain fluorine in higher amounts (0.015-0.030%).

## **VIII. Packaging, Storage and Brewing**

In the country in which the teas are grown, they are cleaned of coarse impurities, graded by leaf size and then packed in standard plywood chest of 20-50 kg lined with aluminium, zinc or plastic foil. To preserve the tea quality, the foils are sealed, soldered or welded. China, glass or metal containers are also suitable for storing tea. Bags made of parchment or filter paper are filled with metered quantities of tea, are also very common. During storage, tea should be protected from light, heat (less than 30 degrees C) and moisture. Other sources of odour should be avoided during storage too. To brew the tea, hot water (about 95 degree C) is usually poured on the leaves (occasionally swirled) and left for 3-5 minutes. Usually a minimum of 4-6 grams of tea leaves per litre is required and stronger extracts may have more than 10 grams of the leaves per litre. The stimulating effect of tea is primary due to the caffeine present.



## **Conclusion**

This review has investigated the history of this ancient beverage, its production in different parts of the world, its botanical and agricultural characteristics, its manufacturing processes for different types of tea, the numerous way to grade tea quality, the common varieties found in the market, its chemical composition and finally the packaging aspect to prolong its keeping and its drinking quality. This study is by no means exhaustive but would provide, hopefully, the reader, with a basic understanding of tea and appreciate its unique taste better.

## CHAPTER 3 PLASTIC FILMS FOR PACKAGING

### I. Introduction

Packaging requirement often include needs to retain volatile contents within a package or to prevent atmospheric vapors from entering a package. Such needs are traditionally handled by glass or metal containers. With the advent of plastic technology, we are witnessing an evolution of products which are being marketed in flexible plastic packaging, having excellent barrier properties, that fulfill the packaging needs and requirement of many products. This chapter reviews the basic characteristics of the polypropylene and acrylonitrile films, used in this research.

### II. Polypropylene (PP)

Polypropylene is discovered in 1954 by Prof. Giulio Natta, of the Milan Polytechnic Institute. Although similar to polyethylene in some respects, polypropylene has a methyl group attached to the C-C backbone. The CH<sub>3</sub> side groups usually follow a regular pattern, which allows the molecules to line up nearly parallel and pack together in a crystalline pattern. However, approximately 5% of the molecules do not conform to this neat arrangement.

The amount of this amorphous substance in the polypropylene resin determines some of its properties. Some necessary additives are added to prevent the rapid

degradation of the plastics from the effects of oxygen and light. The density of polypropylene at 0.90 makes it the lightest of all plastics. One of the greatest shortcomings of polypropylene is its brittleness at low temperatures. However, its light weight and low cost per pound make it a very useful plastic for packaging purposes.

### **III. Oriented Polypropylene (OPP)**

Biaxially Oriented Polypropylene (BOPP) commonly also known as Oriented Polypropylene (OPP), is the most widely used oriented film for packaging applications. Polypropylene is widely used in flexible packaging of biscuits, snack foods, potato crisps and various bakery products on high speed form-fill-seal machines. By orienting the polypropylene film, the physical properties are improved dramatically. Bi-axially oriented polypropylene (BOPP) is produced by biaxially orienting the film - pulling it in two directions: the machine direction and the transverse direction, to give added strength, stiffness, machineability, barrier and gloss.

**Table 4      Orienting Effects on Polypropylene Film**

<b>Property</b>	<b>Non-Oriented PP</b>	<b>Oriented PP</b>
Modulus	High	Very Low
WVTR	1.0 gms/100in <sup>2</sup> /24hrs/mil	0.35 gms/100in <sup>2</sup> /24hrs/mil
Stiffness	Very Low	High
Propagated Tear Strength	High	Very Low
Heat Sealability	350-450 deg F	No - Distorts
Optics	Excellent	Excellent
Surface Receptivity <sup>1</sup>	Low	Low
Oxygen Barrier	Poor	Poor

Orienting polypropylene results in an extremely stiff, flexible film with outstanding moisture barrier, excellent optics, good flexcrack resistance and tear characteristics. The only problem of OPP is that it has high coefficient of friction, poor surface receptivity and will not heat seal. However, OPP can be modified to eliminate these shortcomings.

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<sup>1</sup> Receptivity to inks, adhesives and coatings.

Three general types of modifications are presently used to remedy the above defects:

- A. Coatings added to provide heat sealability, control coefficient of friction and increase oxygen barrier.
- B. Co-extrusion to provide heat sealability and control coefficient of friction.
- C. Slip modified and treated to control coefficient of friction and provide ink/adhesive receptivity.

- Acrylic Coating

Heat sealable from 215 deg F to 300 deg F

Excellent machineability and coefficient of friction

Excellent surface receptivity

Improved flavor/aroma barrier

- PVDC Coating

Heat sealable from 225 deg F to 300 deg F

Excellent surface receptivity , good machineability

Excellent hot tack and improved oxygen/flavor/aroma barrier.

- Coextrusions/Copolymer

Heat sealable from 230 deg F to 300 deg F

Good surface receptivity

Good machineability

Good hot tack

- Slip Modified and Treated

Good surface receptivity

Low coefficient of friction

Good machineability

Oriented polypropylene was initially developed and sold as a replacement for cellophane. Orientation results in stiffness approaching that of cellophane, and about 300 % improvement in moisture barrier. The high stiffness relates directly to superior machineability. In addition, the physical properties of OPP are unaffected by moisture while cellophane will lose or gain moisture resulting changes in stiffness, size and moisture barrier.

**Table 5          OPP Film Versus Cellophane Film**

<b>Property</b>	<b>OPP</b>	<b>Cellophane</b>
Stiffness/Machineability	Excellent	Excellent
Sealability	Good	Good
Hygroscopic	No	Yes
WVTR	0.35	Variable
Dimensional Stability	Yes	No
Physical Properties	Constant	Extremely Variable
Static	Poor	Fair
Yield	High	Low

Besides being able to be co-extruded, laminated or coated, OPP can be metallised too. Research and development of developing silica- and aluminum oxide coated OPP is currently in progress during the writing of this review. Usage of OPP is expanding as technology has been advancing, especially in terms of barrier and sealant capabilities. Modified atmosphere packaging, (MAP) for instance, is a realm OPP has been able to enter because OPP films can be endowed with the gas barriers need for MAP.

## IV. Acrylonitrile

Nitrile polymers are generically those containing cyano ( $\text{C}\equiv\text{N}$ ) functional group, also called the nitrile group. The commercial development of these materials was due largely to the discovery by Sohio, of a low cost one step process for acrylonitrile (AN) production<sup>2</sup> in 1957. The pure nitrile polymer, polyacrylonitrile (PAN), is 49% nitrile. It is an amorphous transparent polymer with a relatively low glass transition temperature ( $T_g = 87^\circ\text{C}$ ) that provides an outstanding barrier to gas permeation and exceptional resistance to a wide range reagents. The only disadvantage is that it is not melt processable. Degradation occurs at  $438^\circ\text{F}$  ( $220^\circ\text{C}$ ). To overcome this handicap, nitrile polymers are produced using acrylonitrile ( $\text{CH}_2=\text{CHCN}$ ) as a comonomer with other monomers that impart melt processability. Through copolymerisation, the desirable properties can be retained and the undesirable properties can be suppressed. The copolymerisation of acrylonitrile and methyl acrylate in a 75:25 ratio onto a nitrile rubber backbone is the approach BP Chemicals uses in its family of High Nitrile Resins (HNRs), sold under the brand Barex<sup>3</sup>. Because of the inherent brittleness of HNRs, they are usually grafted onto a rubber modifier to impart impact strength to the final product. Barex 210 contains 10% of a nitrile rubber modifier. Barex is used only when other plastics cannot economically provide the properties required or where there is a desire to replace traditional materials such as glass or metal.

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<sup>2</sup> US Patent 2,904,580 (Sept.15, 1959), J.D. Idol (to Standard Oil, Ohio).

<sup>3</sup> David Lainchbury, Barrier Pack 1989.



## CHAPTER 4     METHODOLOGY

### I.     Introduction

Pye, et al.<sup>1</sup> described a continuous or isostatic procedure for measuring the diffusivity properties of plastic films that employed two gas chromatographs connected to a single test cell. The authors were able to study the diffusion of gases as well as organic vapors, through the polymer membrane, with the help of multiple detectors. Niebergall et al<sup>2</sup> also described a method for determining the diffusivity properties of various organic permeant/barrier film system based on the isostatic testing procedure. The apparatus developed by these authors was designed to allow measurement of transmission rates for mixtures or organic vapors through barrier structures as a function of permeant concentration, temperature and relative humidity. Hernandez<sup>3</sup> and Baner<sup>4</sup> also employed an isostatic procedure to determine the permeability of organic penetrants through polymer membranes. Analysis of the permeated vapor was based on gas chromatographic technique with flame ionization detector. The steady-state isostatic permeability is the method recommended to evaluate the barrier properties of polymeric films which are expressed as a permeability coefficient<sup>5</sup>. In

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<sup>1</sup> Pye, DG, Mother, MM, and Pannier. M., J. Applied Polymer Sci. 1976, 20: 1921.

<sup>2</sup> Niebergall, W., Humid, A., and Blochl, W., Lebensm. Wiss U. Technol., 1978, (1):1.

<sup>3</sup> Hernandez, R. J., MS. Thesis, Michigan State University, East Lansing 1984.

<sup>4</sup> Baner, A. L., 13th Annual IAPRI Symposium, Oslo, Norway, 1986.

<sup>5</sup> Hernandez, R.J., Giacini, J.R., and Baner, A.L., J. Plastic Film & Sheeting, 1986 Vol 2, p 187-211.

this experiment, the permeability coefficient, diffusion coefficient and solubility coefficient were determined, using the MAS 2000 Organic Flavor Detector.

## II. Theoretical Consideration

Fick's First Law of Diffusion states that the rate of permeant flow is dependent on the diffusion coefficient and the concentration gradient.  $F_x = -D \frac{dC}{dx}$  where  $F_x$  is the flux or amount of permeant diffusing across unit area in unit time, in  $x$  direction.  $D$  is the diffusion coefficient,  $dC$  is the concentration gradient and  $dx$  is the thickness of the film. The negative sign signifies that the diffusion takes place from a region of higher concentration to a region of lower concentration. Henry's Law states the concentration of the permeant in the plastic membrane is related to the permeant concentration in its gaseous phase.  $C = S \cdot p$ , where  $C$  is the concentration of the permeant in the polymer membrane,  $S$  is the solubility coefficient and  $p$  is the partial pressure of the permeant in the vapor phase.

In an isostatic procedure, the diffusion ( $D$ ) and permeability values are obtained from permeability studies where the transport of a permeant through a polymer membrane is continually monitored. The permeation theory incorporated by the MAS 2000 is based on Fick's First Law, as well as Henry's Law. The steady state permeation coefficient,  $P$ , is assumed to be directly proportional to a material's solubility coefficient,  $S$ , and its diffusion coefficient,  $D$ .  $\{ P = D \times S \}$

However, other parameters such as the organics trapped in the membrane prior to the test (and which are desolving from the material at a steady state when the test is initiated) and the instrumentation lag time, needs to be considered into the permeation characteristics that is occurring during the test. The final equation to describe the mass transport rate through a planer surface is :

$$R_t = B + R C^{1/2} \sum \{ \exp (-k^2 C) \} \text{ for } k = 1, 3, 5... \text{ where,}$$

$$C = 1 / \{ 4D (t - t_0) \} \text{ and}$$

$$R = 4 P / 1.77245$$

$R_t$  is the mass transport rate through a planer surface at time  $t$ .

$B$  is the baseline value associated with organics trapped originally in the film before the test was conducted.

$R$  is a constant associated with the permeation coefficient.

$P$  is the permeation coefficient.

$C$  is the constant associated with the diffusion coefficient.

$D$  is the diffusion coefficient.

$t_0$  is the instrumental lag time.

### **III. Machine & Materials**

#### **A. MAS 2000 Organic Permeation Detector**

##### **1. Introduction**

The newly patented MAS 2000 Organic Permeation Detector is a state of art laboratory instrument, designed to measure the rate at which organic compounds such as flavors and aroma, etc that will permeate, diffuse and solubilise in packaging materials, even at parts per billion concentration. This highly sophisticated system incorporates a flame ionization detector, precise temperature and flow rate control, and a high speed 486 computer, driven by a very powerful yet user-friendly software. The ability of the instrument to perform accelerated testing at elevated temperatures, compared with slower analyses at room temperature, helps to reduce product and package development time and related lab costs. By assisting in package barrier optimization, the instrument also can contribute to packagers' source reduction efforts.

## 2. MAS 2000 Specifications

- Instrument Sensitivity : 120 picograms/ m<sup>2</sup>/ sec, 1 picogram/second, or 1 ppb volumetric.
- Data Sampling Rate : 10 Khz.
- Cell Volume : 16 cc.
- Flow Rate Precision : +/- 0.1 ml/min.
- Temperature Range : ambient to 200 degree Celsius.
- Temperature Precision : +/- 0.05 degree Celsius.
- Material Sample Size : 5 inches X 5 inches (or 13 cm X 13 cm).
- Sample Measurement Area : 12.6 square inches ( or 0.0081 square cm).
- Gas Supply Requirements: pressurized nitrogen, hydrogen and air, two stage regulators 0-100 psi (or 0 to 690 Kpa).
- Dimensions : 26 inches D X 36 inches W X 8 inches H (or 66 cm X 91 cm X 20 cm).
- Approximate Weight : 80 pounds (or 36 kg).
- Computer Requirements : 486 SX, 25 MHz processor, 4 MB memory, 100 MB hard drive.

### **III. B. Chemical**

- Linalyl alcohol or Linalool  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2.\text{C}(\text{CH}_3)(\text{OH})\text{CH}=\text{CH}_2$

Purity 97 %, FW 154.25, Boiling point 194-197 ° / 720 mm, Lot No 04027AF, supplied by Aldrich Chemical Company Inc., Milwaukee, Wisconsin 53233, USA.

### **C. Lipton Yellow Label Tea**

- A blend of the finest Assam and other fine teas selected for strength and flavor. CTC (Extra Strong Extra Flavor), Code No 3/92 C. Lipton India Limited, P44 Hide Road, Calcutta 700 088, India.

### **D. Plastic Films**

Four plastic films were selected for this experiment.

- **QHE** : A coextruded, clear and biaxially oriented polypropylene film, 0.9 gauge thick, with super high gloss. One side is sealable, and the other side is treated to provide excellent printability. It is commonly used to package salty snacks and bakery overwrap.

- **MET HB** : This is an oriented polypropylene vacuum metallised film, 0.7 gauge thick, with high barrier properties. It is used as outer web of laminations.
- **AOH** : This is a two-sided, oriented polypropylene film, acrylic coated on one side and PVOH coated on the other. This film, 0.84 gauge thick, is used only as the outer web of lamination, having the PVOH surfaced buried. This film is designed for gas flushing applications and is excellent at maintaining initial gas concentration level. It also provides superior flavor and aroma barrier.
- **Barex 210** : This is a high barrier film used in the food packaging of products which require retention of volatile flavors and aroma, to ensure freshness. It is a single layer of modified acrylonitrile methylacrylate copolymer. The film is approximately one mil in thickness.

#### IV. Experiment Procedure

The operation of the MAS 2000 Organic Flavor Detector was modeled very similarly to the isostatic method developed by Ruben et al<sup>6</sup>. A schematic diagram of the MAS 2000 Organic Vapor Permeation System and Professor Ruben's

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<sup>6</sup> Ruben J. Hernandez, Jack R. Giacini, A. Lawrence Baner, Journal of Plastic Film & Sheeting, Vol 2, July 1986, p 187-211.

Isostatic Permeation System Test Apparatus is shown in Appendix A and Appendix B respectively.

The power for the computer and the chassis was turned on . The pressures on the gas regulators was opened and set accordingly as described in Appendix C. All the test variables in the Test Parameters & Measurement Menu (File Description, Measurement Parameters, Permeant Parameters and Film Parameters) were entered into the computer. Initiate Measurement was selected from the Test Parameters and Measurement Menu, to start the test. Meanwhile, a film sample of 6.0 inches by 6.5 inches was cut and sandwiched between two paperboard film holders with staples. The actual film area measured or tested (diameter 4 inches or 0.1016 meter) was about 12.56 in<sup>2</sup> or 0.0081 m<sup>2</sup>. The sample was labeled and care was taken to ensure that the film surface was free from dust or any surface imperfection. The sample was inserted between the two cell plates, with the barrier layer facing the back of the unit, towards the detector. Leakage was prevented by isolation of the two chambers from each other by incorporating an elastomeric and compressible Viton O-ring at the front cell (see appendix D). The cell was then closed by employing a constant closing force by hitting the F8 function key. The ignition of the detector was started after a pause of 1000 seconds (to stabilize the gas concentration) by hitting F9 function key.

After a steady baseline was established on the screen, a calibration mode (F5) was entered and the computer would save this signal as zero value for reference. The



instrument was then calibrated by injecting 0.25 cc of the 97% linalool's headspace into the injection port by an air-tight syringe. The computer automatically compared the resulting integration of that response or spike with the number of molecules of permeant in the syringe injection based on the Ideal Gas Law. The Ideal Gas Law states that the pressure of the gas is inversely proportional to its volume and directly proportional to its concentration and the temperature.  $pV = nRT$ , where  $p$  is the pressure,  $V$  is the volume,  $n$  is the concentration,  $R$  is the Universal Gas Constant and  $T$  is the temperature in Kelvin. (Hence, if we know the vapor pressure of the permeant, the volume of gas injected, and the temperature of the test cell, the amount of permeant,  $n$ , can be calculated). When the signal had dropped back to the original steady baseline value, the system would automatically exit the calibration mode and the actual test could begin.

The cell temperature was kept constant by two electric heaters and a constant flow of nitrogen was flowing continuously through the front cell (or upstream side). During the test mode, the  $N_2$  stream in the front cell was replaced with the permeant stream. Simultaneously, a constant flow of nitrogen was also passing through the back cell (downstream side), sweeping the organic permeant molecules from the back cell at a constant rate and conveying them to the detector. The detection system comprised of an Flame Ionization Detector (FID), interfaced to the back cell. At preselected time intervals (every 5 seconds), the amount permeated was tracked and fit to a diffusion curve using the Mass Transport Theory. Based on the shape of the curve, the permeability, diffusion and solubility

coefficients were extrapolated. The transmission rates were monitored continually until steady state conditions were obtained. The computer compared the resulting response with the data obtained during calibration simultaneously and the permeation results were plotted on the screen. The computer received the signal, which was detected by the FID in terms of pico-amps, and converted it in terms of micro-grams/m<sup>2</sup>. hr. A constant concentration of the vapor of linalool was obtained using a midjet bubbler to bubble nitrogen gas through the liquid permeant. A fume hood was used for the necessary exhaust. The aroma from the tea leaves was obtained by passing nitrogen gas through a drying tube containing the black tea leaves and channeling the resulting vapor into the front cell of the MAS 2000. To obtain a lower vapor concentration, the permeant vapor stream was mixed with another stream of pure gas carrier. Function key F3 was hit when the testing had been completed. The experiment would require at least 2 film samples of each material; one for interaction with linalool and the other for the black tea. Overall, eight testings were done for linalool and 8 testings for black tea. By plotting  $1/k$  ( $k$ = temperature in Kelvin) versus  $\ln P$  ( $P$ = permeability) to yield a Arrhenius linear plot, the MAS system was able to project permeation values at different temperatures. Hence, different temperatures were tested for each film sample.

## CHAPTER 5 RESULTS & DISCUSSION

The main purpose of this study is to evaluate the permeation characteristics of linalool and black tea flavors in four different films, namely, QHE (Coextruded BOPP), MET-HB (Sealant/High-Energy-Layer/PP/Al), AOH (Acrylic/Adhesive/PP/Adhesive/PVOH) and Barex 210 (Acrylonitrile). A summary of the results can be seen in Tables 6 to 13. The full set of permeation curves and results are shown in Figures 1 to 33.

**Table 6 Permeation Characteristics of Linalool in QHE Film (refer to figures 1-5).**

Temperature	60° C	70°C	80°C	Projection at 22°C
Permeation ugms.mil/m <sup>2</sup> .hr	3844.32	6140.46	9076.62	609.8979
Diffusion mil.mil/hr	0.42887	0.86711	1.29277	0.044741
Solubility ugms/mil.m <sup>2</sup>	8963.83	7081.47	7021.02	13631.63

**Table 7 Permeation Characteristics of Black Tea Flavors in QHE Film (figures 6-9).**

Temperature	80° C	100°C	Projection at 22°C
Permeation umls.mil/m <sup>2</sup> .hr	0.001386	0.007086	0.000003
Diffusion mil.mil/hr	0.879980	1.862202	0.069565
Solubility umls/mil.m <sup>2</sup>	0.001576	0.003805	0.000055

PS: Data at 90°C was unretrievable due to faulty disk

**Table 8 Permeation Characteristics of Linalool in MET-HB Film (figures 10-14).**

Temperature	50° C	60°C	70°C	Projection at 22°C
Permeation ugms.mil/m <sup>2</sup> .hr	97.4761	370.362	479.549	12.08062
Diffusion mil.mil/hr	0.07944	0.14128	0.37327	0.012243
Solubility ugms/mil.m <sup>2</sup>	1227.00	2621.31	1284.71	986.6612

**Table 9 Permeation Characteristics of Black Tea Flavors in MET-HB Film (please refer to figures 15-22)**

Temperature	80° C	90°C	100°C
Permeation umls.mil/m <sup>2</sup> .hr	<= 0.00165	0.002548	<= 0.00157
Diffusion mil.mil/hr	<= 0.99337	0.518209	<= 1.7586
Solubility umls/mil.m <sup>2</sup>	NA	0.004918	NA

**Table 10 Permeation Characteristics of Linalool in AOH Film (figures 23-25).**

Temperature	100°C
Permeation ugms.mil/m <sup>2</sup> .hour	Less than 0.262998
Diffusion mil.mil/hour	Less than 2.276118

**Table 11 Permeation Characteristics of Black Tea Flavors in AOH Film (fig 26-27).**

Temperature	100 <sup>0</sup> C
Permeation umls.mil/m <sup>2</sup> .hour	0.000278
Diffusion mil.mil/hour	0.017379
Solubility umls/mil.m <sup>2</sup>	0.016008

**Table 12 Permeation Characteristics of Linalool in Barex Film (figures 28-30).**

Temperature	100 <sup>0</sup> C
Permeation ugms.mil/m <sup>2</sup> .hour	Less than 0.224155
Diffusion mil.mil/hour	Less than 1.672365

**Table 13 Permeation Characteristics of Black Tea Flavors in Barex Film (fig 31-33).**

Temperature	100 <sup>0</sup> C
Permeation umls.mil/m <sup>2</sup> .hour	0.007827
Diffusion mil.mil/hour	0.019085
Solubility umls/mil.m <sup>2</sup>	0.410111

### **Analysis of Data (Tables 6-13)**

**Table 6 (QHE/Linalool)** showed that as the temperature was increased from 60°C to 80°C, the permeation rate of linalool was increased by approximately 2.36 times (from 3,844 to 9,076 ugms.mil/m<sup>2</sup>.hr). The diffusion rate was increased by approximately 3.07 times (from 0.42 to 1.29 mil.mil/hr). However, the solubility coefficient decreased by 0.78 times from 8963 to 7021 ugms/mil.m<sup>2</sup> when the temperature was increased from 60°C to 80°C. Hence organic flavor loss would still be occurring through scalping, even though the product may be kept under low temperature distribution and/or storage. Higher temperature would result in higher diffusion and permeation rates, which would also result in higher flavor losses (see **figure 4** : Permeation Coefficient, Diffusion Coefficient and Solubility Coefficient of Linalool Versus Temperature). If QHE film would to be used to package any flavored product, temperature where the package is going to be subjected to, must be considered as the product's shelf life would be inevitably affected by the loss of flavor or aroma.

**Table 7 (QHE/BlackTea)** showed that as the temperature increased from 80°C to 100°C, the permeation rate of black tea flavors increased approximately 5.07 times (from 0.0014 to 0.0071 umls.mil/m<sup>2</sup>.hr). The diffusion rate was increased approximately 2.11 times, from 0.8800 to 1.8622 mil.mil/hr. The solubility rate was also increased by about 2.38 times, from 0.0016 to 0.0038 umls/mil.m<sup>2</sup>. This differed from the permeation characteristics of linalool in QHE film in the fact that with an increase in temperature, the permeation rate, diffusion rate and solubility rate of black tea flavors increased (see **figure**

**8** : Permeation coefficient, Diffusion coefficient and Solubility coefficient of Black Tea Flavors versus Temperature).

**Table 8 (MET-HB/Linalool)** showed that as the temperature was increased from  $50^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ , the permeation rate was increased 3.81 times, from 97 to 370 ugms.mil/m<sup>2</sup>.hr. Diffusion rate was increased approximately 1.75 times, from 0.08 to 0.14 mil.mil/hr. The solubility rate increased by 2.13 times, from 1227 to 2621 ugms/mil.m<sup>2</sup>. From  $60^{\circ}\text{C}$  to  $70^{\circ}\text{C}$ , the permeation rate increased by 1.30 times, from 370 to 480 ugms.mil/m<sup>2</sup>.hr. The diffusion rate increased by 2.64 times, from 0.14 to 0.37 mil.mil/hr. However, the solubility rate actually decreased by 0.49 times, from 2621 to 1285 ugms/mil.m<sup>2</sup>. This was particularly interesting as it seemed that between  $60^{\circ}\text{C}$  and  $70^{\circ}\text{C}$ , the linalool molecules were gaining much more kinetic energy or excitement to diffuse out of the membrane than merely staying solubilised in the plastic film.

Studying the temperature range from  $50^{\circ}\text{C}$  to  $70^{\circ}\text{C}$ , the permeation rate was increased approximately 4.94 times, from 97 to 480 ugms.mil/m<sup>2</sup>.hr. The diffusion was increased by 4.65 times, from 0.08 to 0.37 mil.mil/hr. The overall solubility was increased 1.05 times, from 1227 to 1284 ugms/mil.m<sup>2</sup>. **Figure 13** showed a plot of an increase of the solubility coefficient estimate with respect to temperature increase.

**Table 9 (MET-HB/BlackTea)** showed that as temperature increased, from  $80^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , the diffusion rate of black tea flavors also increased from less than 0.99 to about 1.75 mil.mil/hr. The results of the other permeation characteristics could be more conclusive if the test had been conducted for a longer period of time.

**Table 10 (AOH/Linalool)** showed that the permeation was less than 0.26 ugms.mil/m<sup>2</sup>.hr even though it was tested at 100<sup>0</sup>C. More time was needed to establish the solubility coefficient. **Table 11 (AOH/BlackTea)** showed that the permeation, diffusion and solubility coefficient, 0.0003 umls.mil/m<sup>2</sup>.hr, 0.0174 mil.mil/hr and 0.0160 umls/mil.m<sup>2</sup>, respectively, was very minute, also at 100<sup>0</sup>C. **Table 12 (Barex/Linalool)** showed that the permeation was less than 0.2241 ugms.mil/m<sup>2</sup>.hr at 100<sup>0</sup>C. This permeation rate was lower than AOH/Linalool pair. **Table 13 (Barex/BlackTea)** showed that the permeation was approximately 0.0078 umls.mil/m<sup>2</sup>.hr at 100<sup>0</sup>C.

### **Discussion of Permeation Curves (Figures 1 - 33)**

**Figures 1, 2 and 3** showed the permeation curves of linalool in QHE film at 60<sup>0</sup>C, 70<sup>0</sup>C and 80<sup>0</sup>C, respectively. This film, QHE, was selected purposefully, to study how other coated or metallised films would perform ,in terms of acting as an aroma barrier. All the three permeation curves rose from the baseline steadily and proceeded up the permeation curve rather rapidly. Another interesting note was that the half-life (half the time to reach steady state diffusion) decreased with the increase in temperature. The half-life at 60<sup>0</sup>C was 15.71 minutes, whereas the half-life at 70<sup>0</sup>C was only 5.21 minutes. **Figures 4 and 5** showed the temperature analysis plot to obtain regression based on the data collected from the three temperatures tested, to project the permeation characteristics at room temperature. The closer the tested temperature range was to the room temperature, the more precise this projection.



**Figures 6 and 7** showed the permeation curves for black tea flavors in QHE film at 80°C and 100°C respectively. Unfortunately the data at 90°C was lost and could not be retrieved due to a faulty disk. The permeation rates and results were very much lower as compared to the permeation of linalool in QHE film (figures 1,2 and 3).

However, it should be noted that the quantity of organic volatiles which were present in the tea leaves were of a much lower concentration than when we were testing for linalool (which was fully saturated with the linalool vapor from the midjet bubbler). The room temperature projection was obtained based on the two temperatures tested (**figures 8 and 9**). However, in this case, no error estimate of the prediction could be generated from the computer due to insufficient data points (minimum three temperatures required). **Table 14** summarized the figures 1-9, of the permeation characteristics of linalool and black tea flavors with QHE film at room temperature.

**Table 14 Permeation Characteristics with QHE Film at Room Temperature (22°C).**

<b>Permeant</b>	<b>Linalool</b>	<b>Black Tea Flavors</b>
<b>Permeation</b>	<b><math>6 \times 10^{-2}</math> ugms.mil/m<sup>2</sup>.hr</b>	<b><math>3 \times 10^{-6}</math> umls.mil/m<sup>2</sup>.hr</b>
<b>Diffusion</b>	<b><math>4.5 \times 10^{-2}</math> mil.mil/hr</b>	<b><math>7 \times 10^{-2}</math> mil.mil/hr</b>
<b>Solubility</b>	<b><math>1.4 \times 10^4</math> ugms/mil.m<sup>2</sup></b>	<b><math>5.5 \times 10^{-5}</math> umls/mil.m<sup>2</sup></b>

**Figures 10, 11 and 12** showed the permeation curves of Linalool in MET-HB film (metallised) at 50°C, 60°C and 70°C respectively. Figure 10 showed that linalool took 51.31 minutes to reach half-life with the metallised film at 50°C. At 70°C (figure 12), it took 10.92 minutes to reach the half-life, compared with 7.77 minutes for linalool with QHE (figure 2) at the same temperature. This showed that metallised OPP film did offer barrier to organic flavor in some good extent, as shown in **Table 15**. **Figure 13** displayed the temperature analysis of linalool with respect to the permeation, diffusion coefficients and solubility coefficient estimate. This showed that the increase in temperature increased all the permeation coefficients. **Figure 14** showed the data necessary for the Arrhenius Fit room temperature projection and the permeation data at 22°C.

**Table 15 Comparison of the Permeation Characteristics of Linalool with QHE Film and MET-HB Film at Room Temperature (22°C).**

<b>Linalool ( 22°C )</b>	<b>QHE Film</b>	<b>MET-HB Film</b>
<b>Permeation</b>	609.8979 ugms.mil/m <sup>2</sup> .hr	12.08062 ugms.mil/m <sup>2</sup> .hr
<b>Diffusion</b>	0.044741 mil.mil/hr	0.012243 mil.mil/hr
<b>Solubility</b>	13631.63 ugms/mil.m <sup>2</sup>	986.6612 ugms/mil.m <sup>2</sup>

**Figure 15** showed the permeation curve of the black tea flavors with MET-HB film at 80°C. **Figure 16** examined the permeation profile of figure 15 with the zoom-in magnification feature. **Figure 17** was the noise level plot during the testing. Due to the minute level of volatiles present in the black tea sample, a longer duration of testing was recommended to collect more permeation data. **Figure 18** showed the signal analysis of black tea flavors with MET-HB film at 90°C. The half-life was 7.87 minutes. **Figure 19** showed the permeation profile during the test. **Figure 20** showed the permeation curve of black tea with MET-HB film at 100°C. **Figure 21** was the magnification of figure 20. **Figure 22** was the noise level plot during the test mode at 100°C. Again, more time was recommended in the test mode even though figure 20 showed a rather steady state permeation curve. It appeared that all the test of black tea flavors with MET-HB were

flawed since the vapor pressure was continuously dropping over time. Gas Chromatography (GC) to track the concentration of the black tea over time was recommended to further understand, investigate and compare the permeation results and characteristics obtained from the MAS 2000 Organic Flavor Detector. Unfortunately, the gas chromatography instrument (GC) was not available at the Mas Laboratory during that time when conducting these experiments. It was also suggested that perhaps testing with other major volatiles with MAS be included to study the product/package interaction further.

**Figure 23** showed the permeation curve of linalool with AOH film at 100<sup>0</sup>C. **Figure 24** magnified the signal response of the MAS 2000 of figure 23. This temperature was chosen because this film was claimed to be an excellent barrier film and if it would to be tested at room temperature, it would take too long a period. **Figure 25** showed the noise plot during the test. More time was recommended at the test mode to stabilize the data. No projection of permeation at room temperature was generated as a minimum of two temperature data points were needed. **Figure 26** showed the magnified permeation curve of black tea with AOH film at 100<sup>0</sup>C. **Figure 27** showed its signal analysis with a half-life of 337.77 minutes. **Table 16** summarized the permeation characteristics of linalool and black tea flavors with AOH film at 100<sup>0</sup>C.

**Table 16 Permeation Characteristics with AOH Film at 100°C.**

<b>Permeant</b>	<b>Linalool</b>	<b>Black Tea Flavors</b>
<b>Permeation</b>	Less than $2.6 \times 10^{-1}$ ugms.mil/m <sup>2</sup> .hr	$2.78 \times 10^{-4}$ umls.mil/m <sup>2</sup> .hr
<b>Diffusion</b>	Less than $2.27 \times 10^0$ mil.mil/hr	$1.74 \times 10^{-2}$ mil.mil/hr

**Figure 28** showed the permeation curve of linalool with Barex film at 100°C. Noticed the sharp rise of the curve in the initial start-up. This could be due to the dust particles or trapped organics within the film. **Figure 29** magnified the permeation curve of figure 28. **Figure 30** showed the noise plot. The high noise could be attributed to temperature fluctuations occurring at the high cell temperature of 100°C. The test could have been prolonged further to obtain more permeation data points to construct the projected permeation curve. **Figure 31** showed the permeation curve of black tea flavors with Barex at 100°C. **Figure 32** was the magnification of figure 31. **Figure 33** showed the actual and projected permeation data. The half-life was 435.91 minutes. **Table 17** summarized the permeation characteristics of linalool and black tea flavors with Barex film at 100°C.

**Table 17 Permeation Characteristics with Barex Film at 100°C.**

<b>Permeant</b>	<b>Linalool</b>	<b>Black Tea Flavors</b>
<b>Permeation</b>	Less than $2.2 \times 10^{-2}$ ugms.mil/m <sup>2</sup> .hr	$7.8 \times 10^{-3}$ umls.mil/m <sup>2</sup> .hr
<b>Diffusion</b>	Less than $1.67 \times 10^0$ mil.mil/hr	$1.9 \times 10^{-2}$ mil.mil/hr

### **Discussion of Permeation Results**

The data collected showed that there was a difference in the barrier property of the four films to linalool. The QHE film seemed to yield the highest permeation rate than the other three films, for the permeant linalool. The MET-HB film yielded the second highest permeation rate. The AOH film and Barex film could be considered to be very good flavor barrier packaging material as the permeation rates were rather low even at 100°C. The actual permeation value for AOH and Barex film at room temperature would be significantly lower, and hence would unlikely to affect the product quality in terms of linalool loss. More testings should be done for the AOH and Barex with linalool at two or more other temperatures to obtain the regression plot at room temperature. Though these testing at lower temperatures would take much longer time than when tested at 100°C, the data collected would help complete the data and enable better comparison with the other films' performance at room temperature. No conclusion about which of the two films

(AOH and Barex) had the best flavor barrier property for the permeant linalool could be made at this juncture until more testings had been performed and the data analyzed.

The permeation data collected for black tea flavors with the four plastic films was more complicated than the permeation data for linalool. Firstly, there was insufficient data to enable comparison of the permeation characteristics at room temperature. However, for the sake of discussion, 100°C was selected for comparison as there were testings conducted for each of the four films at this temperature. However, it must be noted that this temperature may be above the glass transition of the plastic films and hence, the permeation characteristics at a lower temperature would be much different from the that at 100°C. Also it must be noted that using the data collected from the accelerated testing of the film sample at 100°C alone, was dangerous as it inevitably increased the rate of diffusion and hence might yield a lower solubility coefficient for the permeant/membrane pair. It must also be understood that interference caused by the interactions of the many other organic components present in the tea leaves with the plastic film could also affect the permeation characteristics of the major tea flavor component, linalool. Nonetheless, from the available data collected from this experiment, MET-HB seemed to have the lowest black tea flavor permeation rate, followed by AOH, QHE and Barex film. A duplicate test to verify the permeation characteristics of the black tea flavors with MET-HB for a longer period of time at room temperature and at two other temperatures was suggested before any conclusive remark can be made at this time. The permeation of black tea flavors in QHE and Barex is about the same but the half-life for Barex was 436

minutes, (figure 33) compared to QHE, the half life was only 3.6 minutes (figure 7). Hence, the diffusion rate of QHE will be many times faster than Barex film. The author had, also conducted a personal sensory evaluation of four samples of tea packaged in each plastic film, kept for about 18 months at room temperature. The author was able to detect tea flavor migration into the headspace of the glass jar through the sense of smell for the QHE film and the MET-HB film. Unfortunately, it was not possible to quantify the amount present in the headspace of these jars by smelling. The author was not able to detect any tea flavor in the headspace of the glass jar for the AOH and Barex film. The discrepancy between the migration of the black tea flavor from the tea package to the headspace of the glass for the MET-HB film, with the analytical result from the MAS 2000 could be due to the presence of pin holes in the package, flexing of the film during the cutting, sealing and filling operations.

## **Conclusion**

The permeation characteristics of linalool and black tea flavors were evaluated in the four plastic films, namely , the QHE film, the MET-HB film , the AOH film and the Barex film. The MAS 2000 Organic Flavor Detector was able to detect linalool and the minute volatile components present in the black tea leaves. The data collected suggested that each film has a different barrier property to linalool and the black tea flavors. The relationship between the permeation characteristics of linalool and the black tea flavors in the four plastic films could not be established at this present time as more data are needed to verify the permeation profile in each film.

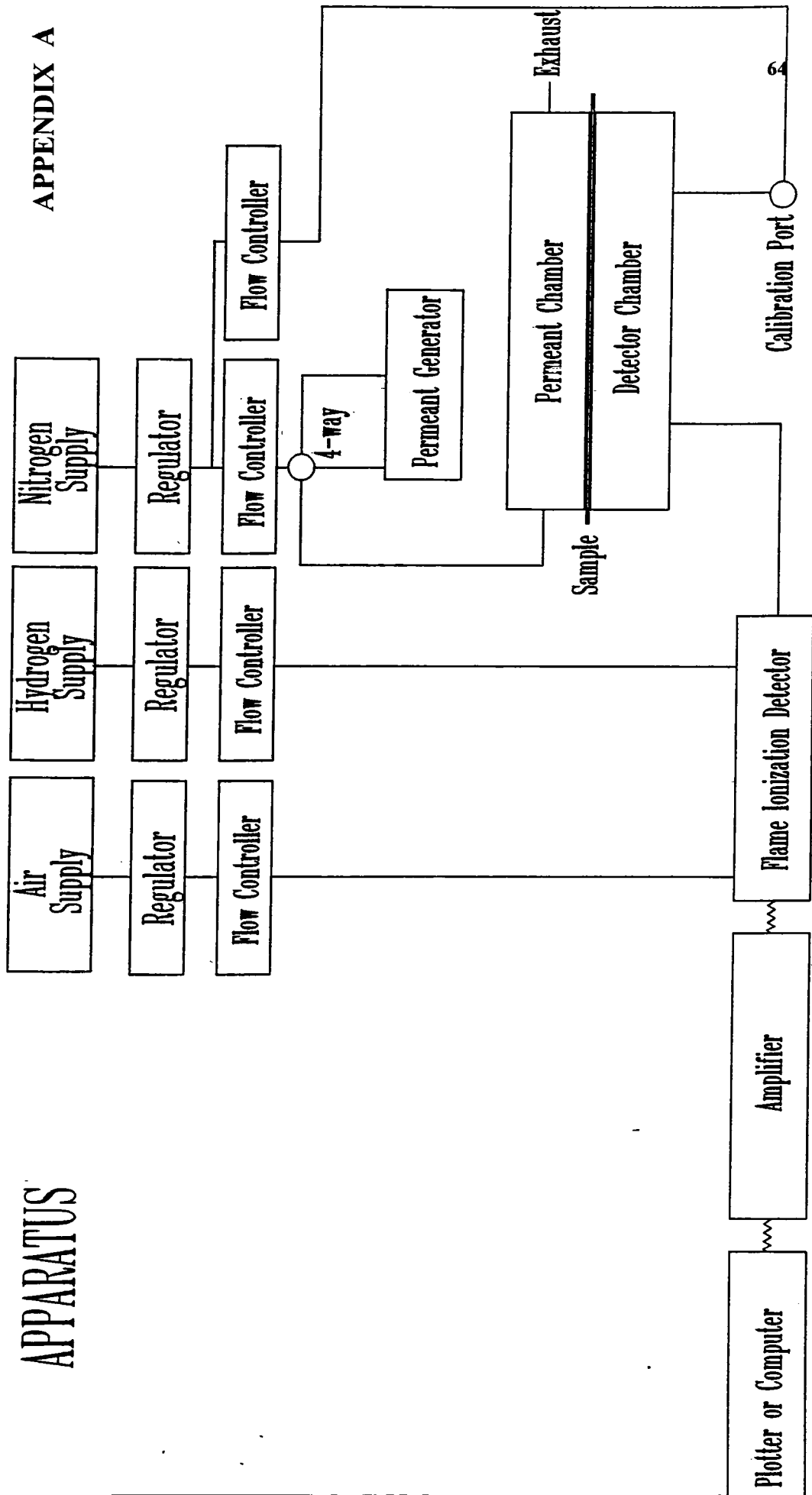


## **Recommendations for Future Research**

All the data collected for this research made use of only one single calibration file ( file 0524BXA) and this input was transferred into all the permeation curves. The author would suggest that each plastic film has its own calibration file for each permeant at each temperature setting. Especially for the calibration for the testing of the black tea flavors, the headspace of the black tea leaves should be used (instead of using linalool). The above recommendations seek to eliminate any potential differences or variances from sample to sample, film to film and/or temperature to temperature. For easy comparison, testing at preselected temperatures (temperatures that the package would likely to be exposed to, such as 30<sup>0</sup>C, 40<sup>0</sup>C, 50<sup>0</sup>C or 60<sup>0</sup>C) should be the applied for all the plastic films to allow more accurate projection of the film's performance in real life application. This would also give a better projection of the permeation at 22<sup>0</sup>C. Other brand of black tea samples could also be experimented to verify the barrier property of the four plastic films. As more and more tea are blended with other flavors and spices (eg peppermint, lemon and cinnamon), flavor barrier property of the packaging material will become an increasingly important issue, in determining the product's quality, acceptance and success.

# APPARATUS

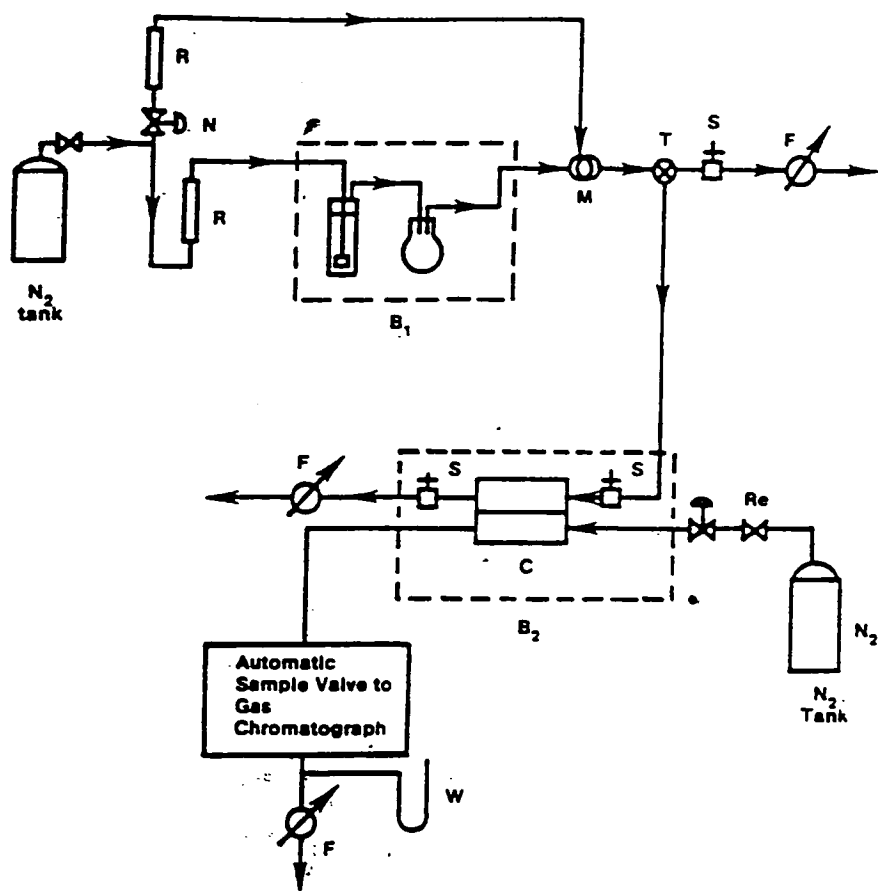
## APPENDIX A



## APPENDIX B

### SCHEMATIC OF ISOSTATIC PERMEATION TEST APPARATUS

(Professor Ruben Hernandez)



- B<sub>1</sub> - Water bath, generation of permeant vapor phase diluted in Nitrogen
- B<sub>2</sub> - Water bath ( $\pm 0.1^\circ\text{C}$ )
- C - Cell
- F - Gas flow bubble meter
- M - Mixing device
- N - Needle valve
- R - Rotameter
- Re - Regulator
- S - Sample port
- T - Three way valve
- W - Water manometer

## Appendix C

Recommended Regulator Pressure Values For MAS 2000 Organic Flavor Detector, Serial Number 1994005:

Hydrogen ..... 14-18 psi

Air ..... 70-74 psi

Nitrogen ..... 22-26 psi

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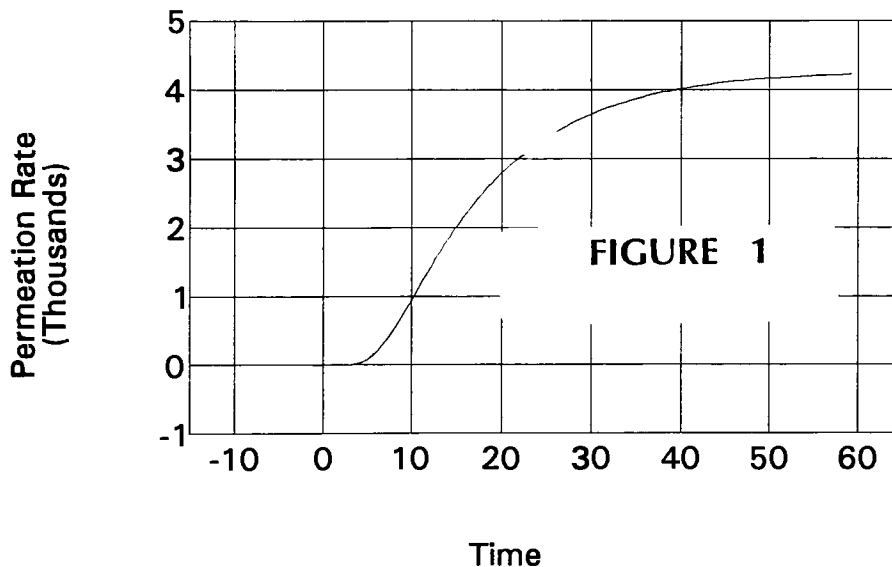
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Time:	<b>13:15:43</b>

Material:	<b>QHE</b>
Caliper (mils):	<b>0.9</b>

Permeant:	<b>Linalool</b>
PPM V	<b>412</b>

Temperature (deg c):	<b>60</b>
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**Permeation Data  
Actual and Projected**



Time Units: **minutes**  
Permeation Rate Units: **ugms/m2.hour**

**Parameter Estimates**

Baseline (pico amperes):  
Steady State Permeation:  
Diffusion (1/hours):

Value	Std. Error	% error
<b>14.01213</b>	<b>0.105208</b>	<b>0.750837</b>
<b>4271.47</b>	<b>17.54562</b>	<b>0.410763</b>
<b>0.529469</b>	<b>0.003430</b>	<b>0.647889</b>

Half Life: **15.71283 minutes**

**Material Coefficients**

Permeation	<b>3844.323 ugms.mil/m2.hour</b>
Diffusion	<b>0.428870 mil.mil/hour</b>
Solubility	<b>8963.831 ugms/mil.m2</b>

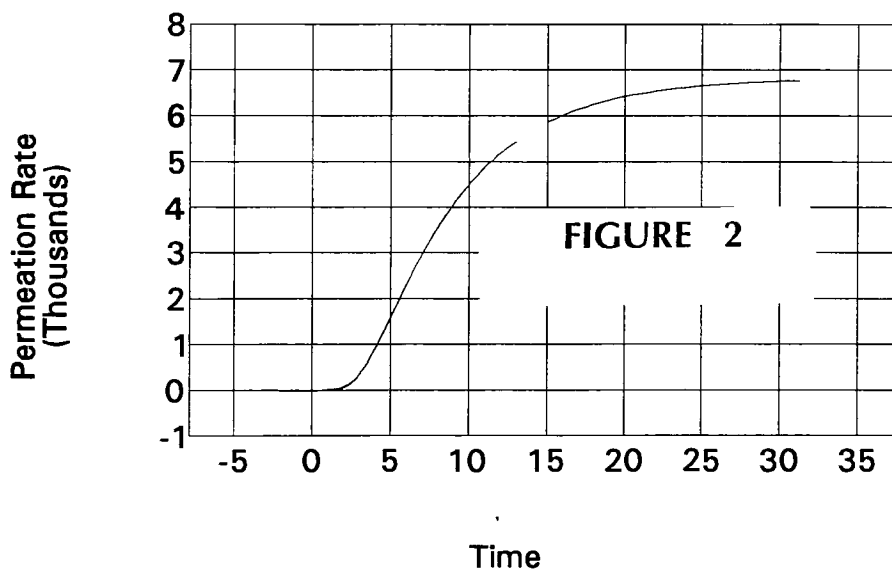
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Material:	<b>QHE</b>
Caliper (mils):	<b>0.9</b>

Permeant:	<b>Linalool</b>
PPM V	<b>412</b>

Temperature (deg c):	<b>70</b>
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**Permeation Data  
Actual and Projected**



Time Units: **minutes**  
Permeation Rate Units: **ugms/m2.hour**

**Parameter Estimates**

Baseline (pico amperes):  
Steady State Permeation:  
Diffusion (1/hours):

Value	Std. Error	% error
<b>12.39498</b>	<b>0.186139</b>	<b>1.501734</b>
<b>6822.737</b>	<b>22.42887</b>	<b>0.328737</b>
<b>1.070514</b>	<b>0.006629</b>	<b>0.619239</b>

Half Life: **7.771465 minutes**

**Material Coefficients**

Permeation	<b>6140.463 ugms.mil/m2.hour</b>
Diffusion	<b>0.867116 mil.mil/hour</b>
Solubility	<b>7081.470 ugms/mil.m2</b>



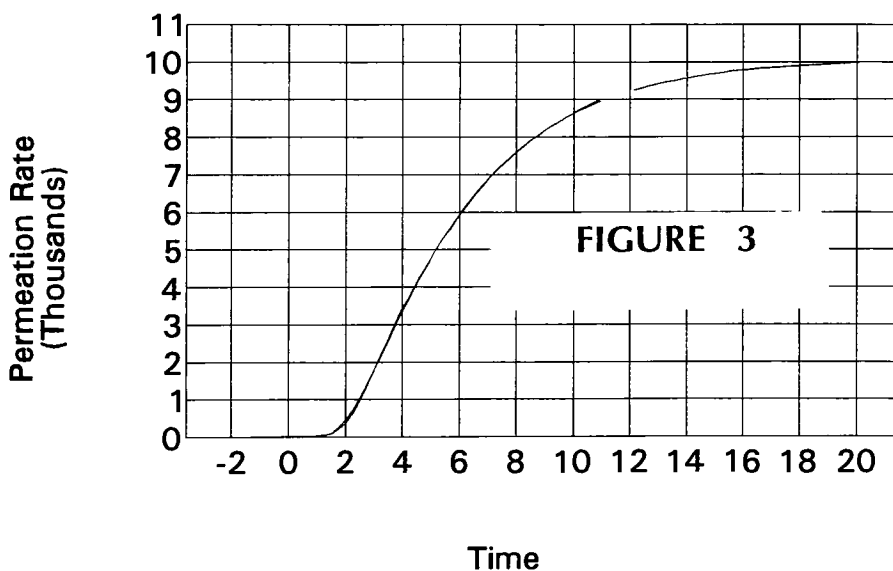
File:	<b>0525QHEB</b>
Date:	<b>05-25-94</b>
Time:	<b>13:10:32</b>

Material:	<b>QHE</b>
Caliper (mils):	<b>0.9</b>

Permeant:	<b>Linalool</b>
PPM V	<b>412</b>

Temperature (deg c):	<b>80</b>
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**Permeation Data  
Actual and Projected**



Time Units: **minutes**  
 Permeation Rate Units: **ugms/m2.hour**

**Parameter Estimates**

Baseline (pico amperes):  
 Steady State Permeation:  
 Diffusion (1/hours):

Value	Std. Error	% error
<b>19.58038</b>	<b>0.787846</b>	<b>4.023650</b>
<b>10085.14</b>	<b>46.54234</b>	<b>0.461494</b>
<b>1.596023</b>	<b>0.016296</b>	<b>1.021048</b>

Half Life: **5.212624 minutes**

**Material Coefficients**

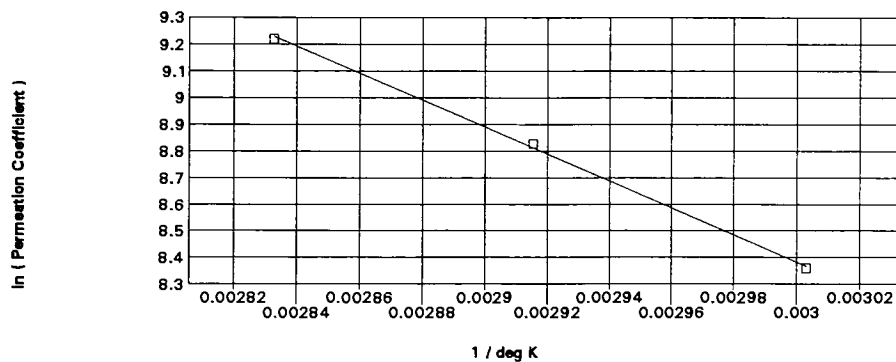
Permeation	<b>9076.626 ugms.mil/m2.hour</b>
Diffusion	<b>1.292778 mil.mil/hour</b>
Solubility	<b>7021.020 ugms/mil.m2</b>

Material:	<i>QHE</i>
Caliper (mils):	<i>0.9</i>

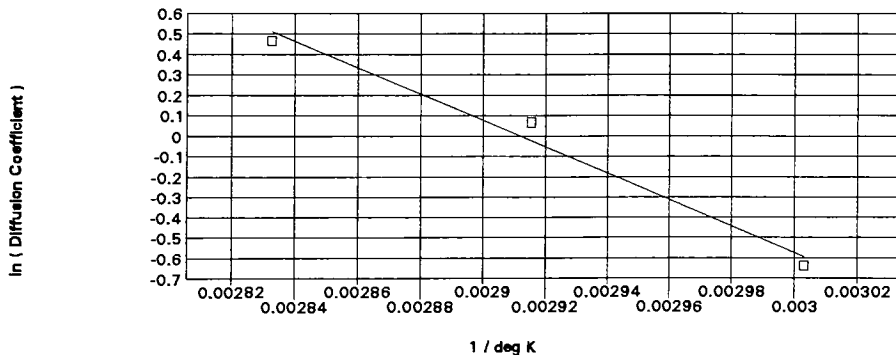
Permeant:	<i>Linalool</i>
Concentration:	<i>1.00</i>

Permeation Units:	<i>ugms/m2.hr</i>
Diffusion Units:	<i>1/hrs</i>
Solubility Units:	<i>ugms/m2</i>

### Permeation Coefficients



### Diffusion Coefficients



### Solubility Coefficient Estimate

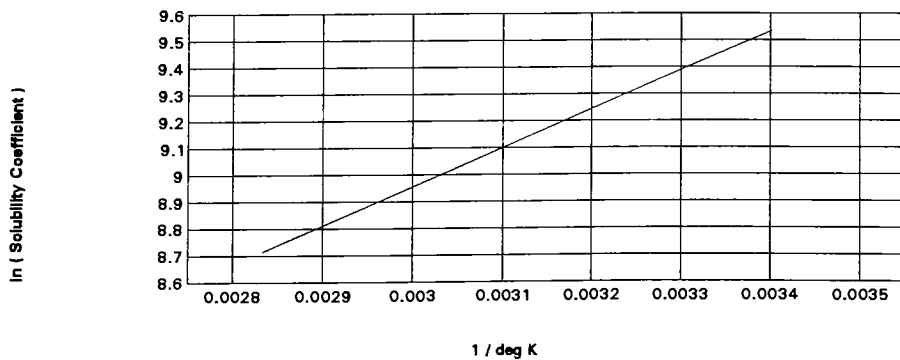


FIGURE 4

Material:	<b><i>QHE</i></b>
Caliper (mils):	<b><i>0.9</i></b>

Permeant:	<b><i>Linalool</i></b>
Concentration:	<b><i>1.00</i></b>

Permeation Units:	<b><i>ugms/m2.hr</i></b>
Diffusion Units	<b><i>1/hrs</i></b>
Solubility Units:	<b><i>ugms/m2</i></b>

**FIGURE 5**

**Arrhenius Fit**  
**Regression Parameters**  
 $\ln(P) = \text{int.} + \text{slp.} / T$

	Intercept	Slope
Permeation	<b><i>23.54359</i></b>	<b><i>-5053.43</i></b>
Diffusion	<b><i>18.93234</i></b>	<b><i>-6501.56</i></b>

**Arrhenius Fit**  
**Room Temperature Projection (22 deg. C)**

Permeation	<b><i>609.8979 ugms/m2.hr</i></b>
Diffusion	<b><i>0.044741 1/hrs</i></b>
Solubility	<b><i>13631.63 ugms/m2</i></b>

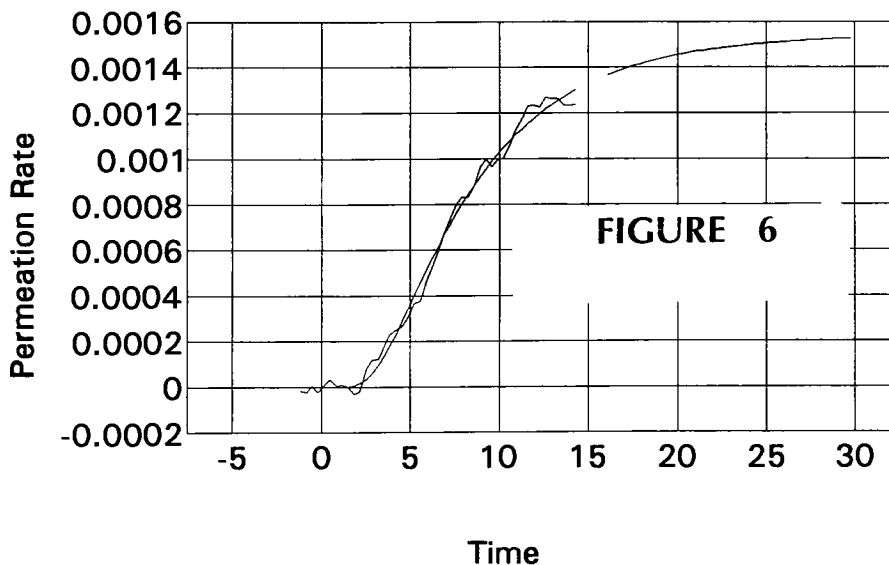
File:	<b>0526QHEA</b>
Date:	<b>05-26-94</b>
Time:	<b>13:22:40</b>

Material:	<b>QHE</b>
Caliper (mils):	<b>0.9</b>

Permeant:	<b>BLACK TEA</b>
PPM V	<b>Unknown</b>

Temperature (deg c):	<b>80</b>
----------------------	-----------

Permeation Data  
Actual and Projected



Time Units: **minutes**  
Permeation Rate Units: **u/mls/m2.hour**

Parameter Estimates  
Baseline (pico amperes):  
Steady State Permeation:  
Diffusion (1/hours):

Value	Std. Error	% error
<b>16.33791</b>	<b>0.014217</b>	<b>0.087023</b>
<b>0.001541</b>	<b>0.007990</b>	<b>518.5371</b>
<b>1.086396</b>	<b>0.074685</b>	<b>6.874576</b>

Half Life: **7.657859 minutes**

#### Material Coefficients

Permeation	0.001386 u/mls.mil/m2.hour
Diffusion	0.879980 mil.mil/hour
Solubility	0.001576 u/mls/mil.m2

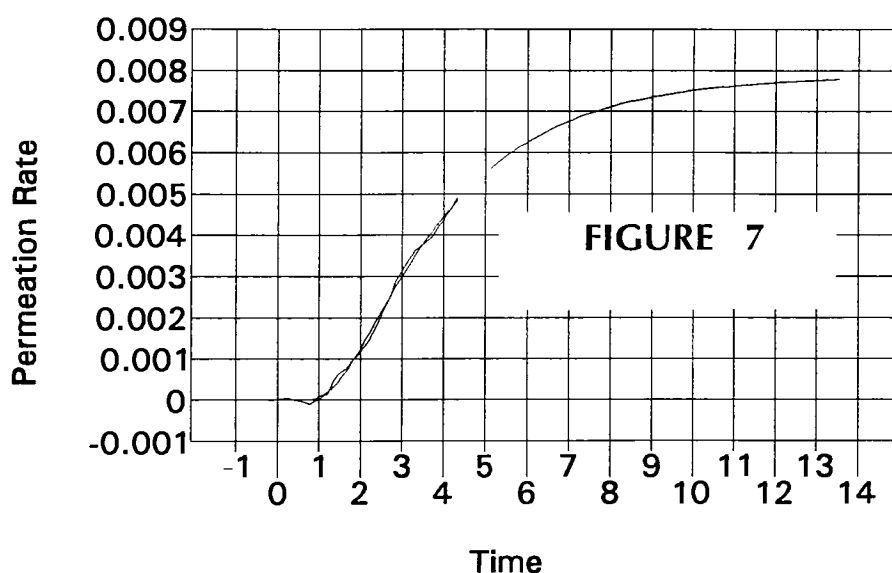
File:	<b>0526QHEC</b>
Date:	<b>05-26-94</b>
Time:	<b>13:52:53</b>

Material:	<b>QHE</b>
Caliper (mils):	<b>0.9</b>

Permeant:	<b>BLACK TEA</b>
PPM V	<b>Unknown</b>

Temperature (deg c):	<b>100</b>
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**Permeation Data  
Actual and Projected**



Time Units: **minutes**  
Permeation Rate Units: **umls/m2.hour**

**Parameter Estimates**
**Baseline (pico amperes):**
**Steady State Permeation:**
**Diffusion (1/hours):**

Value	Std. Error	% error
<b>54.41833</b>	<b>0.032469</b>	<b>0.059665</b>
<b>0.007873</b>	<b>0.062018</b>	<b>787.6945</b>
<b>2.299015</b>	<b>0.154700</b>	<b>6.728971</b>

**Half Life: 3.618710 minutes**
**Material Coefficients**

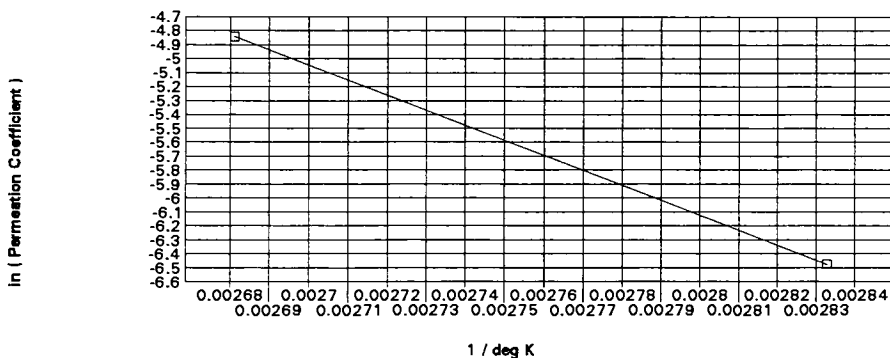
<b>Permeation</b>	<b>0.007086 umls.mil/m2.hour</b>
<b>Diffusion</b>	<b>1.862202 mil.mil/hour</b>
<b>Solubility</b>	<b>0.003805 umls/mil.m2</b>

Material:	<b><i>QHE</i></b>
Caliper (mils):	<b><i>0.9</i></b>

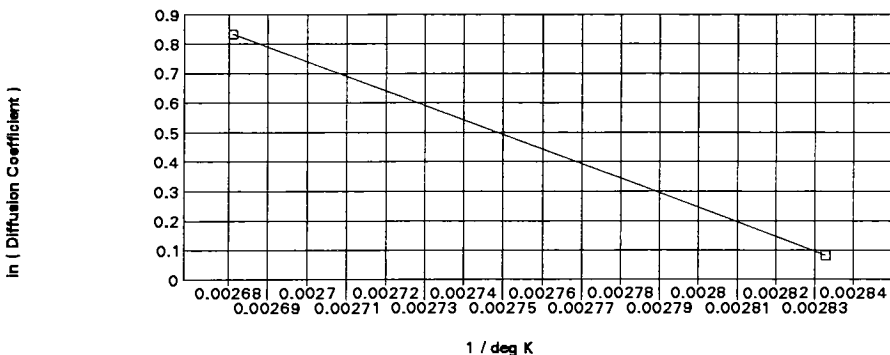
Permeant:	<b><i>BLACK TEA</i></b>
Concentration:	<b><i>1.00</i></b>

Permeation Units:	<b><i>umls/m2.hr</i></b>
Diffusion Units	<b><i>1/hrs</i></b>
Solubility Units:	<b><i>umls/m2</i></b>

### Permeation Coefficients



### Diffusion Coefficients



### Solubility Coefficient Estimate

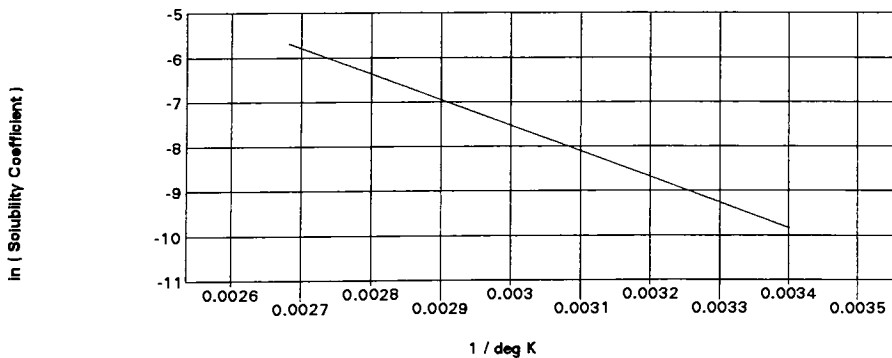


FIGURE 8

Material:	<b><i>QHE</i></b>
Caliper (mils):	<b><i>0.9</i></b>

Permeant:	<b><i>BLACK TEA</i></b>
Concentration:	<b><i>1.00</i></b>

Permeation Units:	<b><i>umls/m2.hr</i></b>
Diffusion Units:	<b><i>1/hrs</i></b>
Solubility Units:	<b><i>umls/m2</i></b>

FIGURE 9

Arrhenius Fit  
Regression Parameters  
 $\ln(P) = \text{int.} + \text{slp.} / T$

Intercept    Slope

Permeation	<b><i>23.94347</i></b>	<b><i>-10737.8</i></b>
Diffusion	<b><i>14.06188</i></b>	<b><i>-4934.57</i></b>

Arrhenius Fit  
Room Temperature Projection (22 deg. C)

Permeation	<b><i>0.000003 umls/m2.hr</i></b>
Diffusion	<b><i>0.069565 1/hrs</i></b>
Solubility	<b><i>0.000055 umls/m2</i></b>

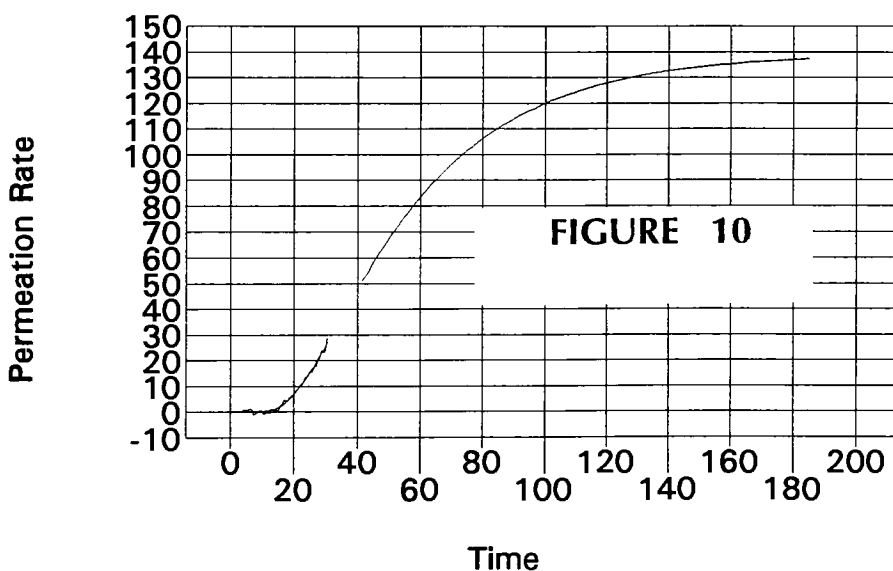
File:	<b>0524META</b>
Date:	<b>05-24-94</b>
Time:	<b>12:57:22</b>

Material:	<b>MET-HB</b>
Caliper (mils):	<b>0.7</b>

Permeant:	<b>Linalool</b>
PPM V	<b>412</b>

Temperature (deg c):	<b>50</b>
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**Permeation Data  
Actual and Projected**



Time Units: **minutes**  
Permeation Rate Units: **ugms/m2.hour**

Parameter Estimates  
Baseline (pico amperes):  
Steady State Permeation:  
Diffusion (1/hours):

Value	Std. Error	% error
<b>11.67187</b>	<b>0.011314</b>	<b>0.096936</b>
<b>139.2516</b>	<b>42.18904</b>	<b>30.29698</b>
<b>0.162127</b>	<b>0.032725</b>	<b>20.18496</b>

Half Life: **51.31440 minutes**

**Material Coefficients**

Permeation	<b>97.47612 ugms.mil/m2.hour</b>
Diffusion	<b>0.079442 mil.mil/hour</b>
Solubility	<b>1227.003 ugms/mil.m2</b>



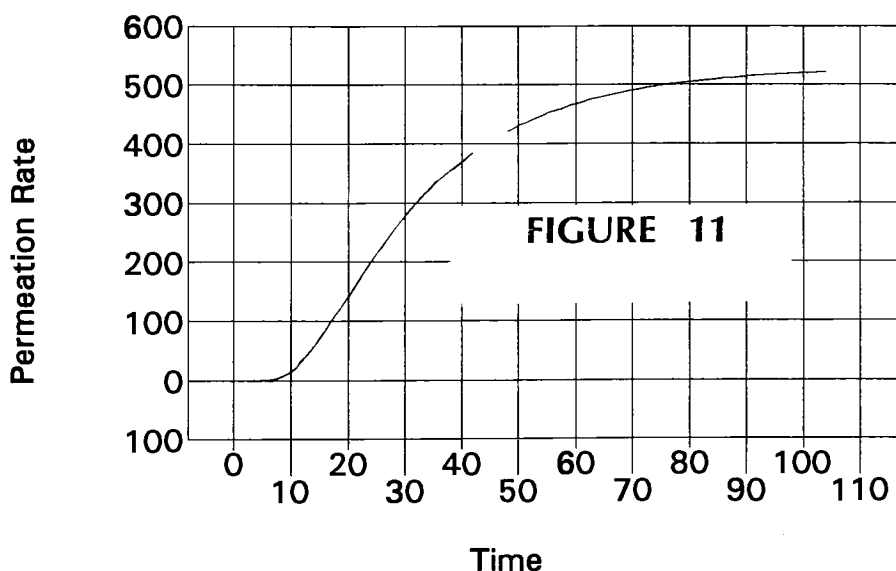
File:	<b>0524METB</b>
Date:	<b>05-24-94</b>
Time:	<b>13:01:26</b>

Material:	<b>MET-HB</b>
Caliper (mils):	<b>0.7</b>

Permeant:	<b>Linalool</b>
PPM V	<b>412</b>

Temperature (deg c):	<b>60</b>
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**Permeation Data  
Actual and Projected**



Time Units: **minutes**  
Permeation Rate Units: **ugms/m2.hour**

#### Parameter Estimates

Baseline (pico amperes):  
Steady State Permeation:  
Diffusion (1/hours):

Value	Std. Error	% error
<b>68.28649</b>	<b>0.034060</b>	<b>0.049878</b>
<b>529.0899</b>	<b>4.17382</b>	<b>0.788867</b>
<b>0.288344</b>	<b>0.003587</b>	<b>1.244110</b>

Half Life: **28.85253 minutes**

#### Material Coefficients

Permeation	<b>370.3629 ugms.mil/m2.hour</b>
Diffusion	<b>0.141288 mil.mil/hour</b>
Solubility	<b>2621.318 ugms/mil.m2</b>

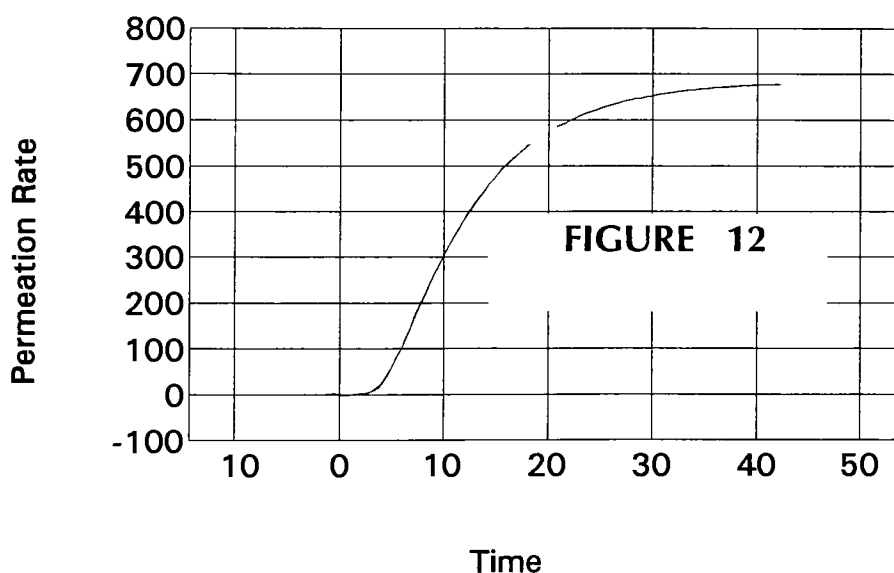
File:	<b>0524METC</b>
Date:	<b>05-24-94</b>
Time:	<b>13:03:40</b>

Material:	<b>MET-HB</b>
Caliper (mils):	<b>0.7</b>

Permeant:	<b>Linalool</b>
PPM V	<b>412</b>

Temperature (deg c):	<b>70</b>
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**Permeation Data  
Actual and Projected**



Time Units: **minutes**  
Permeation Rate Units: **ugms/m2.hour**

**Parameter Estimates**
**Baseline (pico amperes):**
**Steady State Permeation:**
**Diffusion (1/hours):**

Value	Std. Error	% error
<b>38.20811</b>	<b>0.028988</b>	<b>0.075870</b>
<b>685.0713</b>	<b>3.293662</b>	<b>0.480776</b>
<b>0.761785</b>	<b>0.006704</b>	<b>0.880055</b>

**Half Life: 10.92101 minutes**
**Material Coefficients**

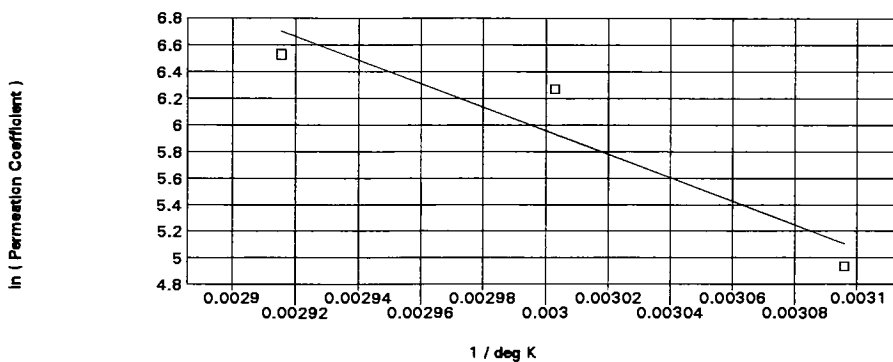
Permeation	<b>479.5499 ugms.mil/m2.hour</b>
Diffusion	<b>0.373274 mil.mil/hour</b>
Solubility	<b>1284.710 ugms/mil.m2</b>

Material:	<b>MET-HB</b>
Caliper (mils):	<b>0.7</b>

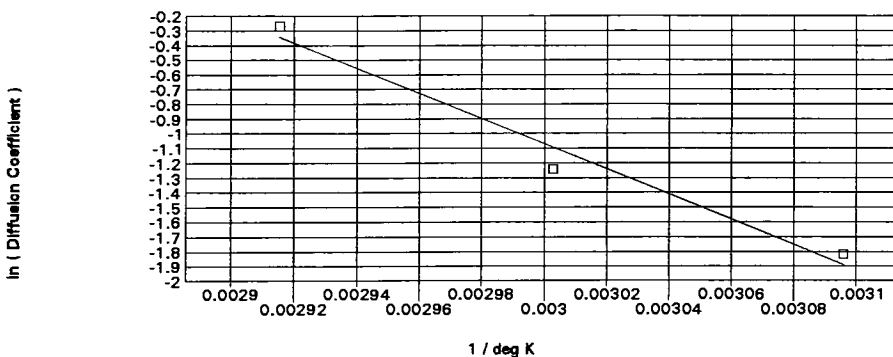
Permeant:	<b>Linalool</b>
Concentration:	<b>1.00</b>

Permeation Units:	<b>ugms/m2.hr</b>
Diffusion Units:	<b>1/hrs</b>
Solubility Units:	<b>ugms/m2</b>

### Permeation Coefficients



### Diffusion Coefficients



### Solubility Coefficient Estimate

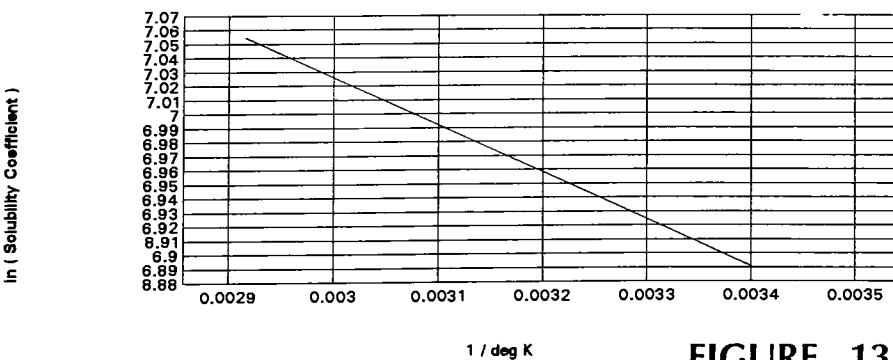


FIGURE 13

Material:	<b><i>MET-HB</i></b>
Caliper (mils):	<b><i>0.7</i></b>

Permeant:	<b><i>Linalool</i></b>
Concentration:	<b><i>1.00</i></b>

Permeation Units:	<b><i>ugms/m2.hr</i></b>
Diffusion Units	<b><i>1/hrs</i></b>
Solubility Units:	<b><i>ugms/m2</i></b>

FIGURE 14

Arrhenius Fit  
Regression Parameters  
 $\ln(P) = \text{int.} + \text{slp.} / T$

	Intercept	Slope
Permeation	<b><i>32.60862</i></b>	<b><i>-8884.52</i></b>
Diffusion	<b><i>24.5725</i></b>	<b><i>-8547.69</i></b>

Arrhenius Fit  
Room Temperature Projection (22 deg. C)

Permeation	<b><i>12.08062 ugms/m2.hr</i></b>
Diffusion	<b><i>0.012213 1/hrs</i></b>
Solubility	<b><i>986.6612 ugms/m2</i></b>

Data File: 0527METC

Calibration File: 0524BXA

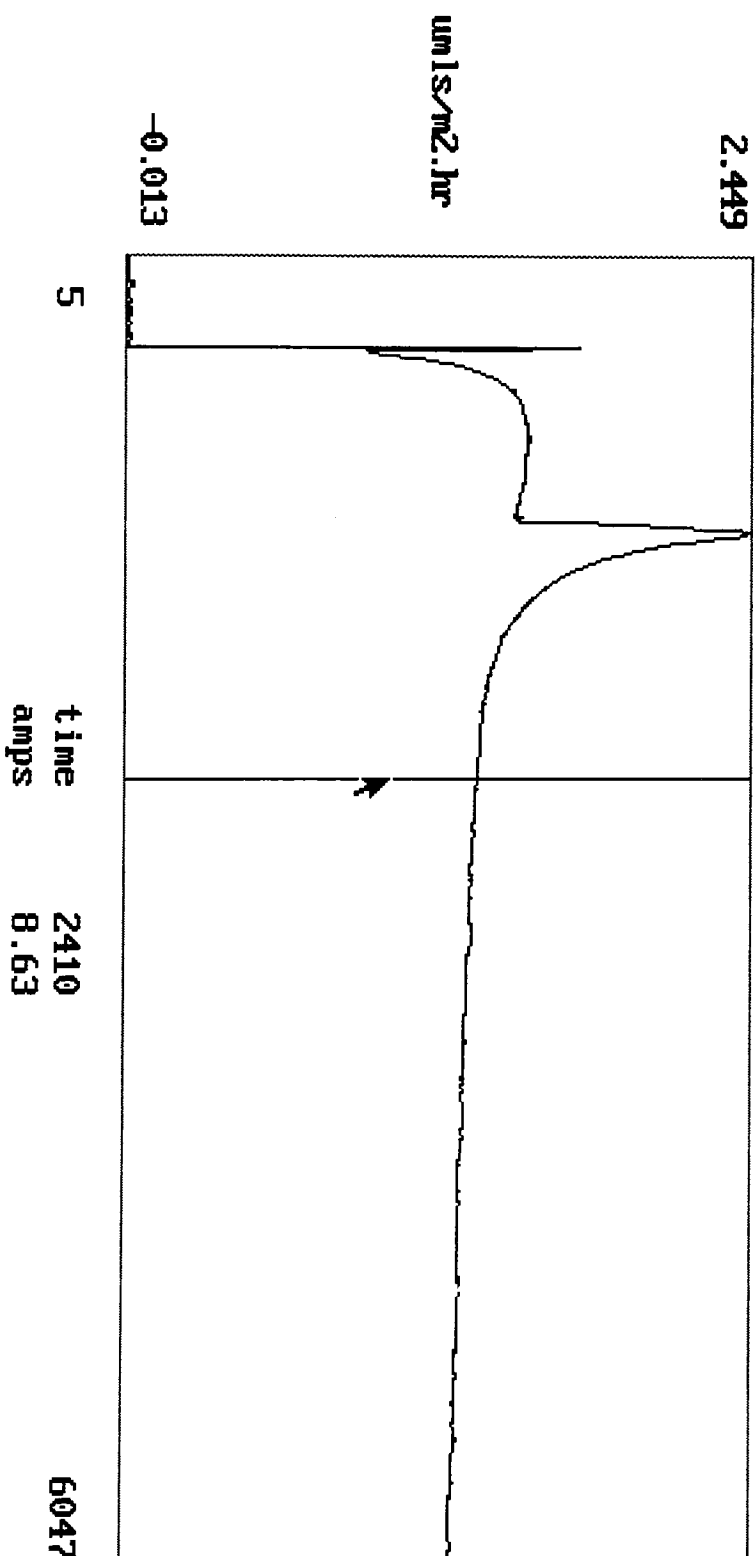
material: MET-HB  
caliper: .7permeant: Black Tea  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 80  
fid temp: 150

FIGURE 15

f1:file f2:edit f3:analysis f4:exit

Data File: 0527METC

Calibration File: 0524BXA

material: MET-HB  
caliper: .7

permeant: Black Tea  
concentration: 1  
vapor pressure: .313  
injection: .25

cell temp: 80  
fid temp: 150

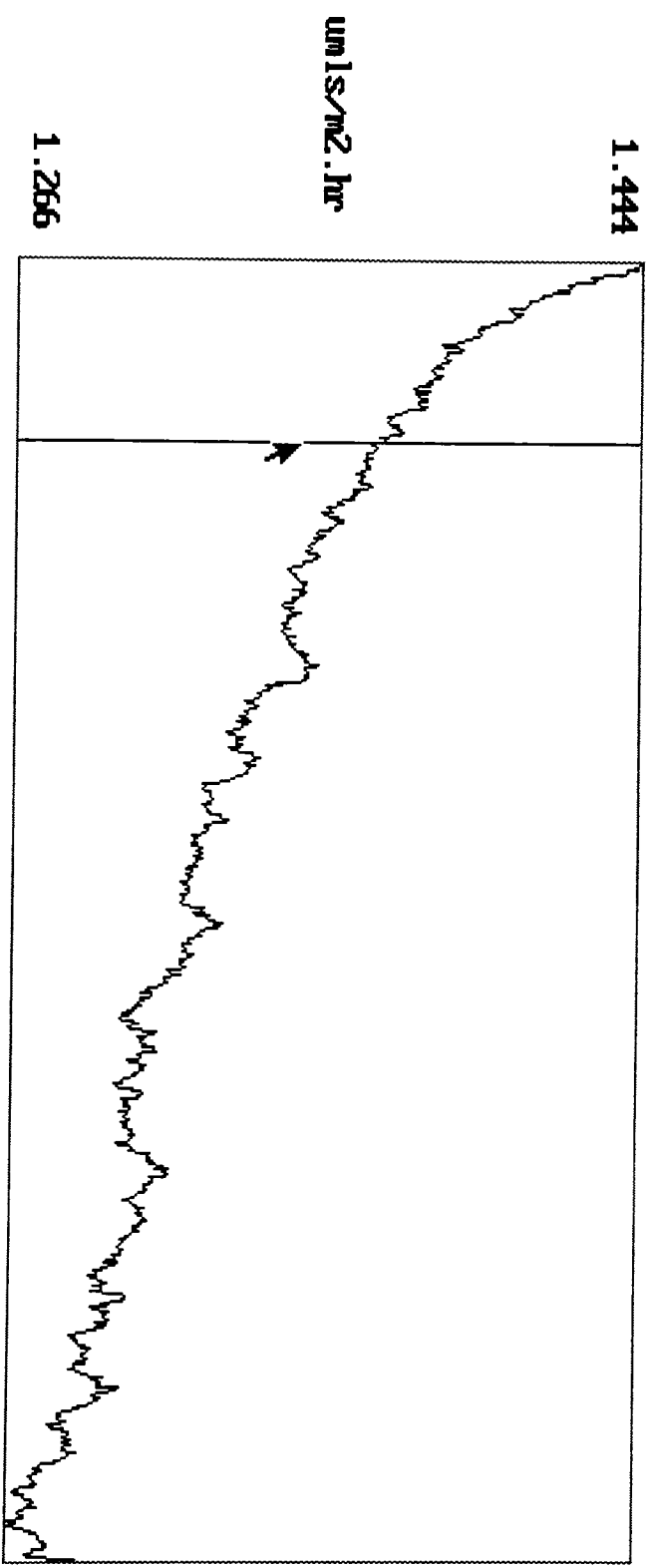


FIGURE 16

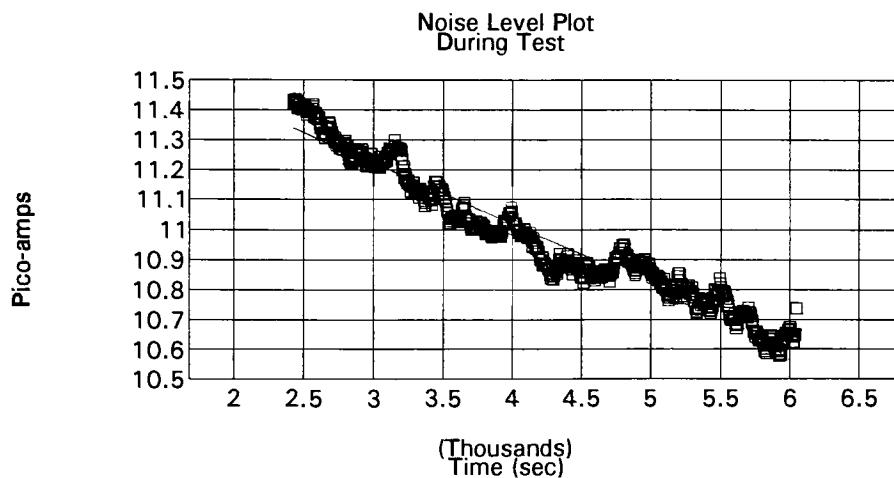
f1:range f2:remove f3:adjust f4:slope f5:subtract f6:prn file f7:exit

1843	time	2423	6047
	amps	11.25	

DATA FILE:	0527METC	UPPER LIMITS
FILM:	MET-HB	
PERMEANT:	Black Tea	

85

Noise	0.949812 Pico-amps
Test Time	3624 sec



Diffusion < =	0.993377 (1/hrs)
Permeation < =	0.001658 micromoles/m2.hr

NOTES:

## FIGURE 17

Recommend conducting a product/package interaction study and MAS2000 testing using the major volatiles found in study.  
Needed more time in test mode.

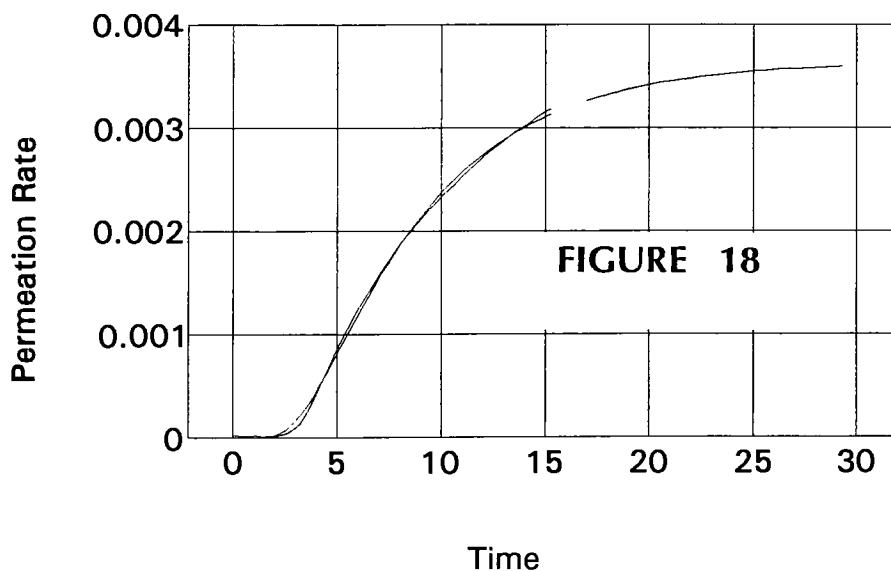
File:	<b>0527METB</b>
Date:	<b>05-27-94</b>
Time:	<b>10:40:55</b>

Material:	<b>MET-HB</b>
Caliper (mils):	<b>0.7</b>

Permeant:	<b>Black Tea</b>
PPM V	<b>Unknown</b>

Temperature (deg c):	<b>90</b>
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Permeation Data  
Actual and Projected



Time Units: **minutes**  
Permeation Rate Units: **u/mls/m2.hour**

#### Parameter Estimates

Baseline (pico amperes):  
Steady State Permeation:  
Diffusion (1/hours):

Value	Std. Error	% error
<b>5.400383</b>	<b>0.015835</b>	<b>0.293234</b>
<b>0.003640</b>	<b>0.006884</b>	<b>189.0907</b>
<b>1.057571</b>	<b>0.026762</b>	<b>2.530605</b>

Half Life: **7.866582 minutes**

#### Material Coefficients

Permeation	0.002548 u/mls.mil/m2.hour
Diffusion	0.518209 mil.mil/hour
Solubility	0.004918 u/mls/mil.m2



Data File: 0527METB

Calibration File: 0524BXA

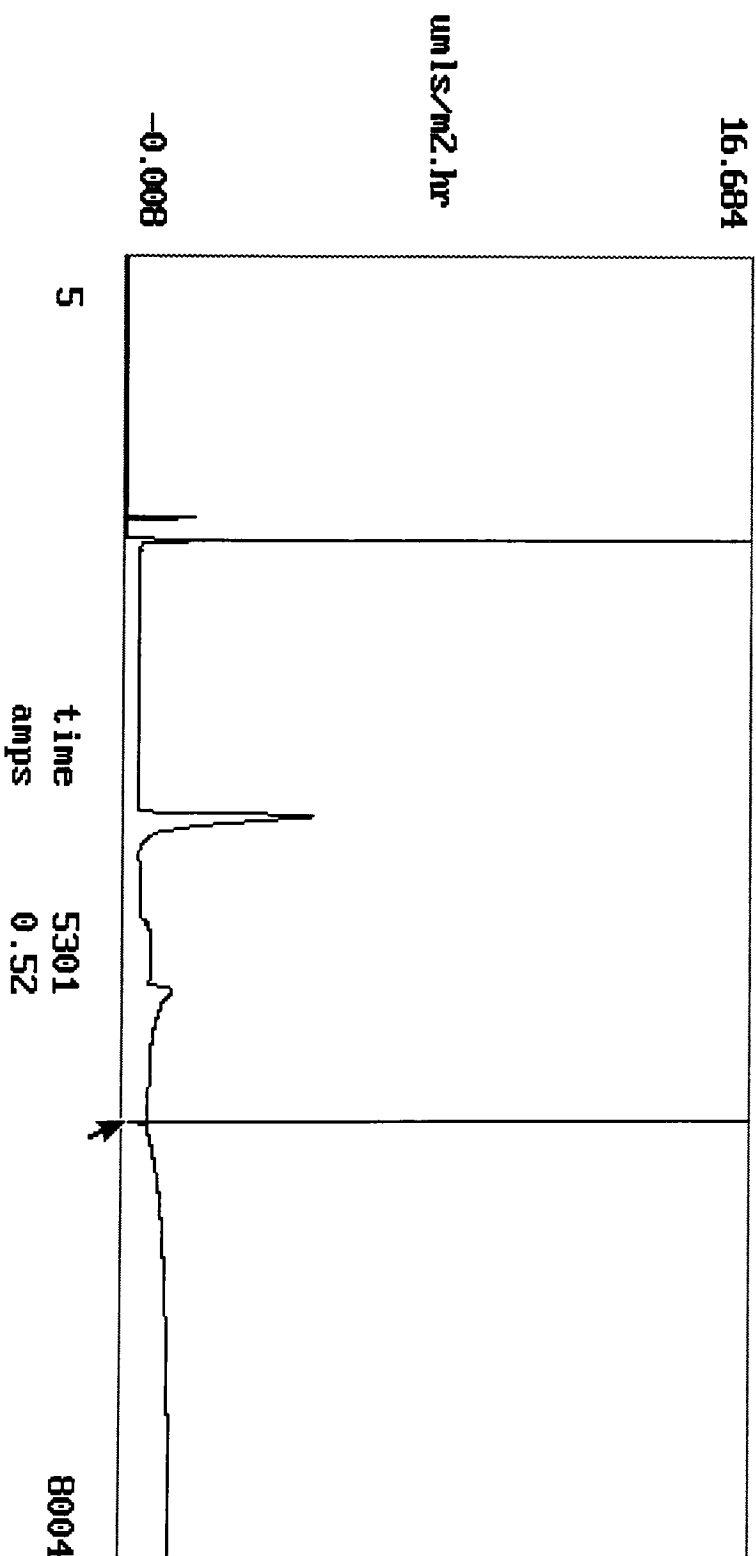
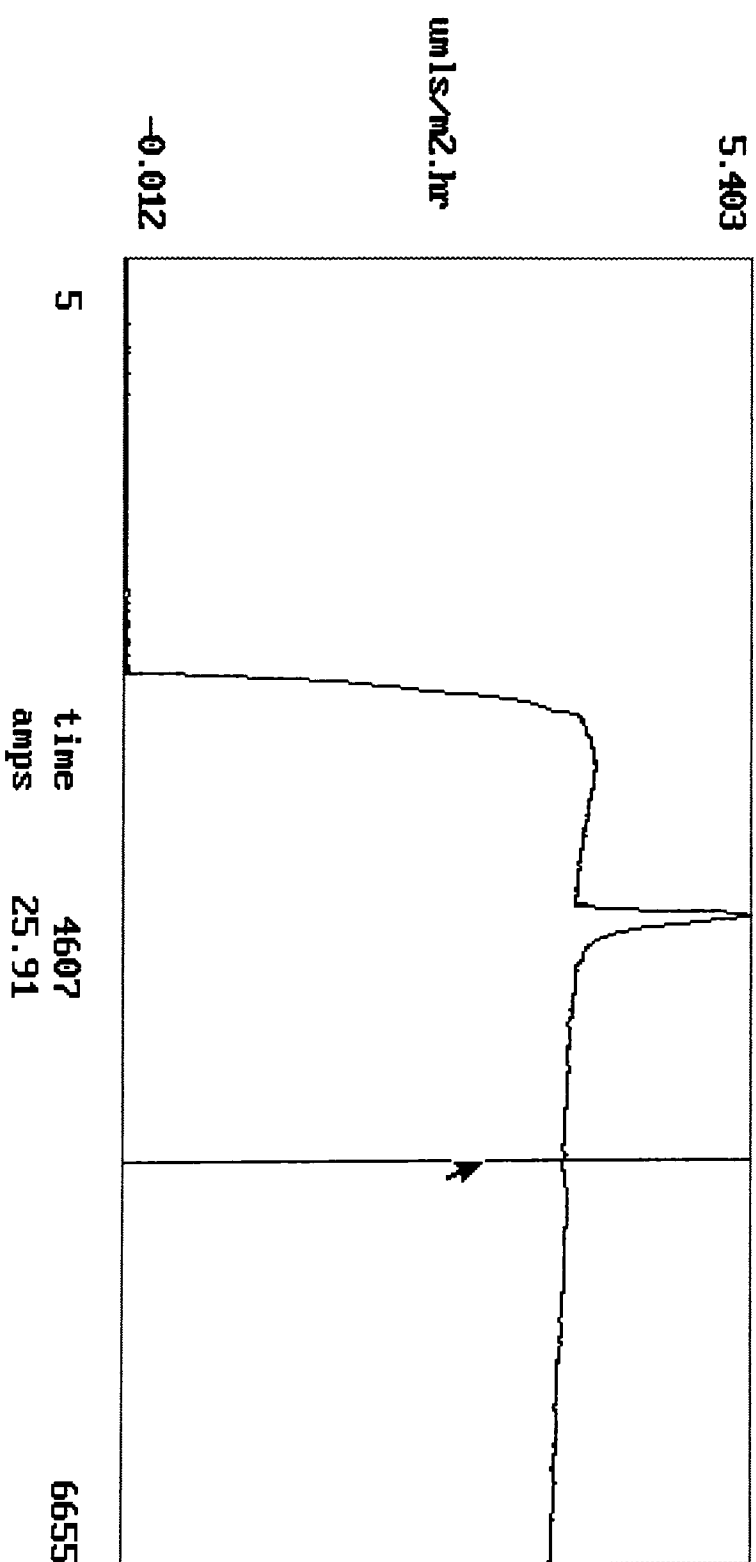
material: MET-HB  
caliper: .7permeant: Black Tea  
concentration: 1  
vapor pressure: .314  
injection: .25cell temp: 90  
fid temp: 150

FIGURE 19

f1:file f2:edit f3:analysis f4:exit

Data File: 0527META

Calibration File: 0524BXA

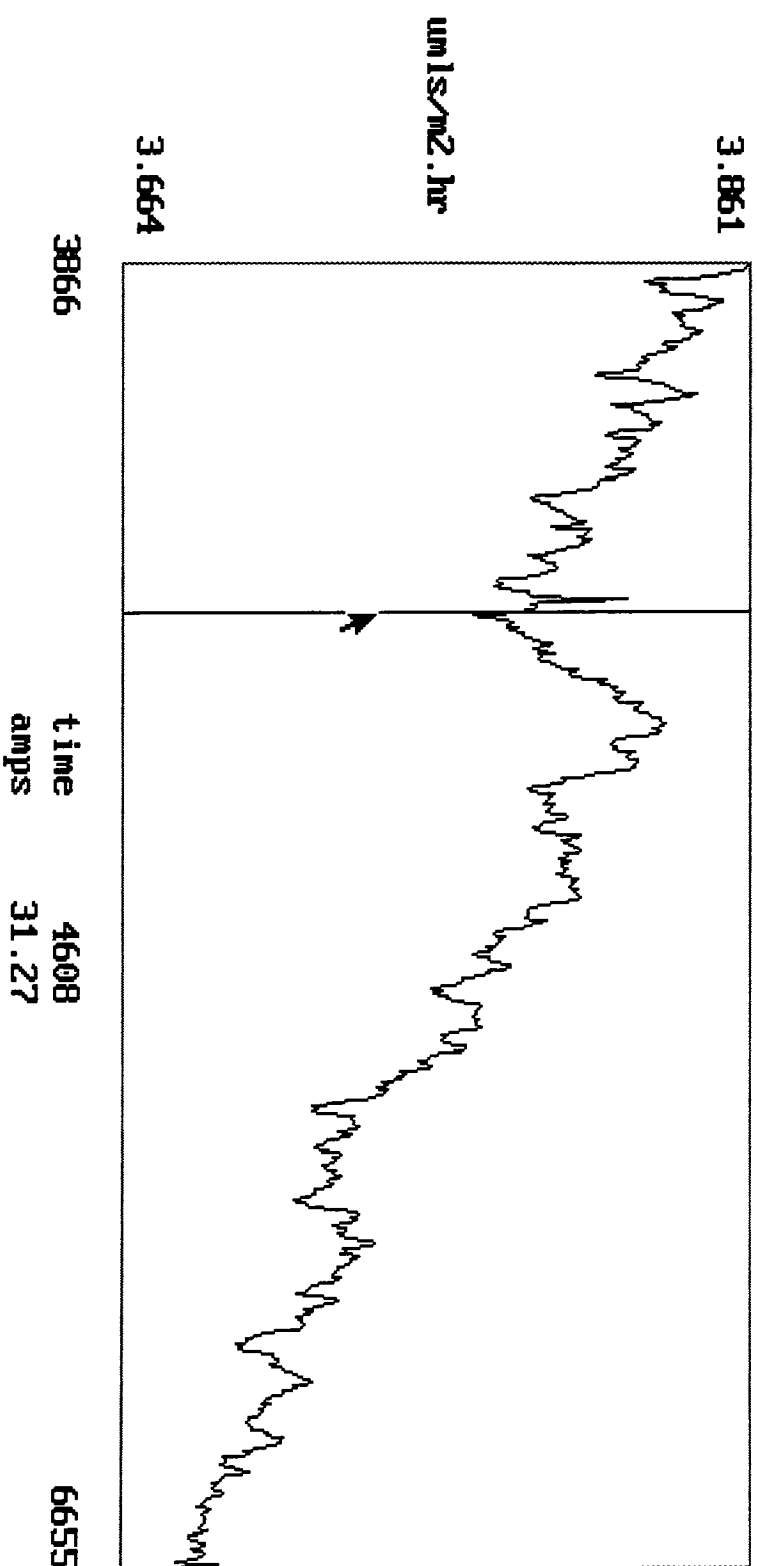
material: MET-HB  
caliper: .7permeant: BLACK TEA  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 150

f1:file f2:edit f3:analysis f4:exit

FIGURE 20

Data File: 0527META

Calibration File: 0524BXA

material: MET-HB  
caliper: .7permeant: BLACK TEA  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 150

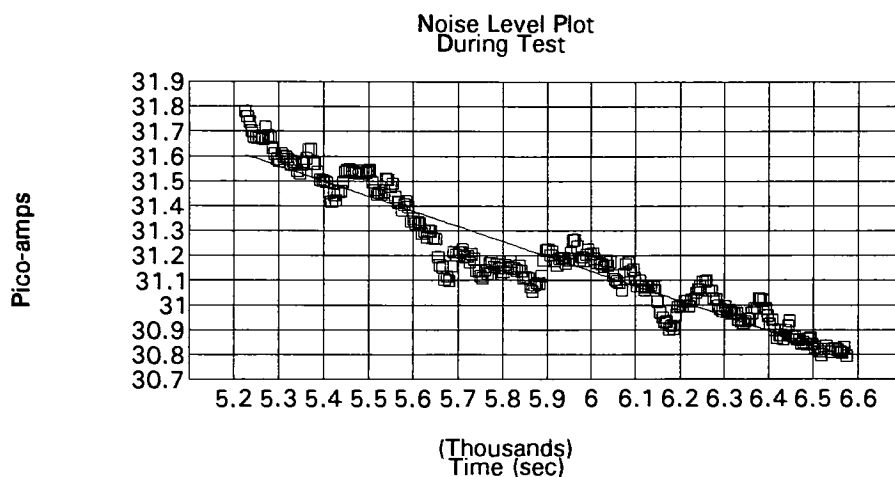
f1:range f2:remove f3:adjust f4:slope f5:subtract f6:prn file f7:exit

FIGURE 21

DATA FILE:	0527META	UPPER LIMITS
FILM:	MET-HB	
PERMEANT:	Black Tea	

90

Noise	0.903281 Pico-amps
Test Time	2047 sec



Diffusion < =	1.758671 (1/hrs)
Permeation < =	0.001576 micromoles/m <sup>2</sup> .hr

**NOTES:** Recommend conducting a product/package interaction study and MAS2000 testing using the major volatiles found in study. Not enough time in Test mode to observe any Permeation.

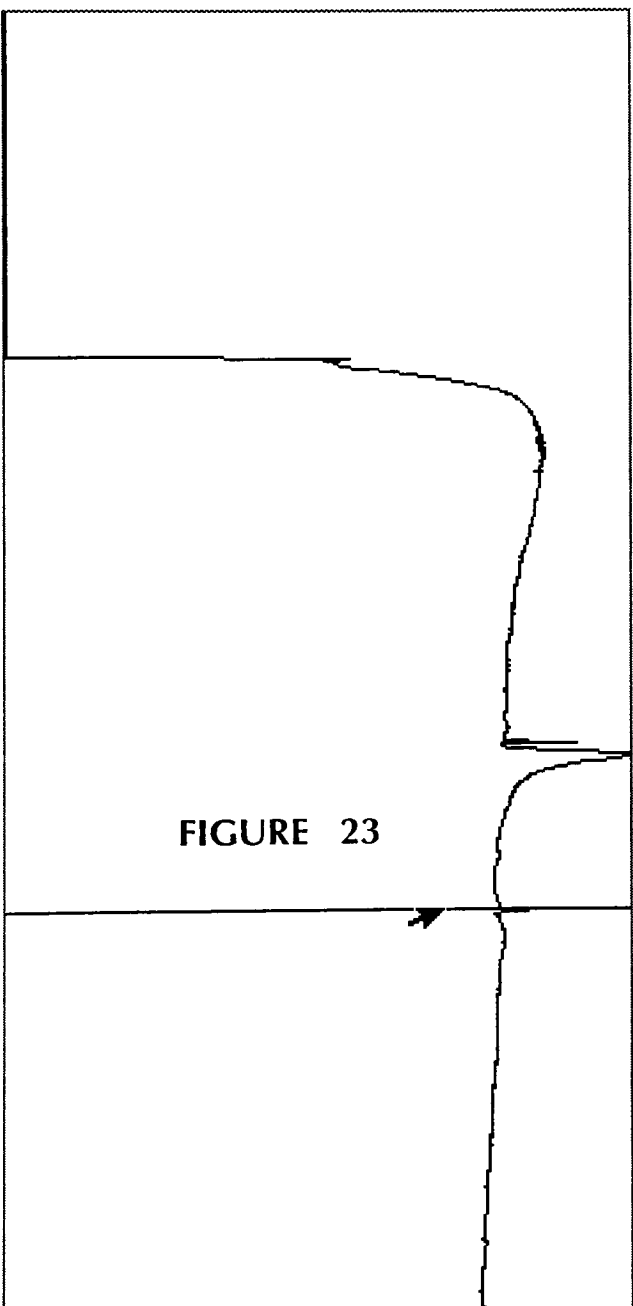
**FIGURE 22**

Data File: 0525A0HA

Calibration File: 0524BXA

material: AOH  
caliper: .84permeant: Linalool  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 1501647.056  
ugms/m2.hr

-1.532

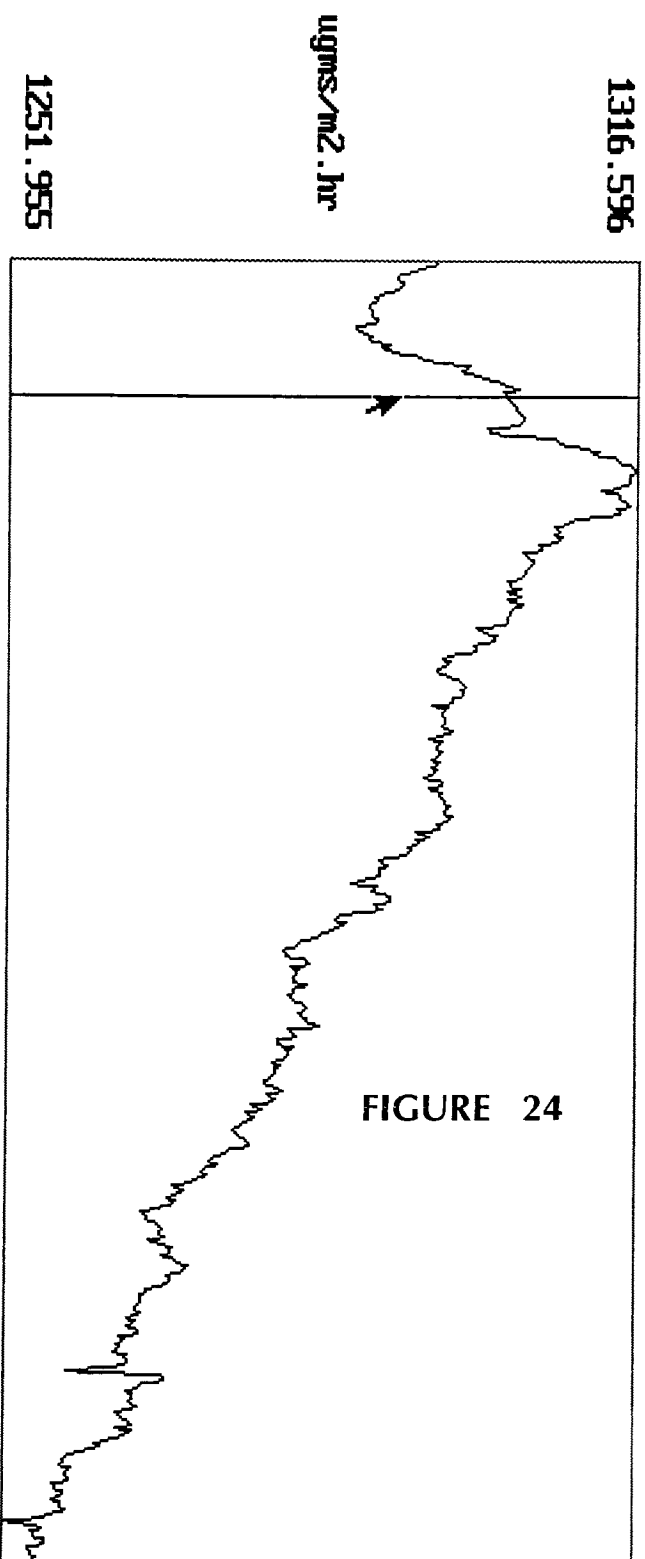


5	time	3665	5309
	amps	62.82	

f1:file f2:edit f3:analysis f4:exit

Data File: 0525A0H.A

Calibration File: 0524B.XA

material: AOH  
caliper: .84permeant: Linalool  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 150

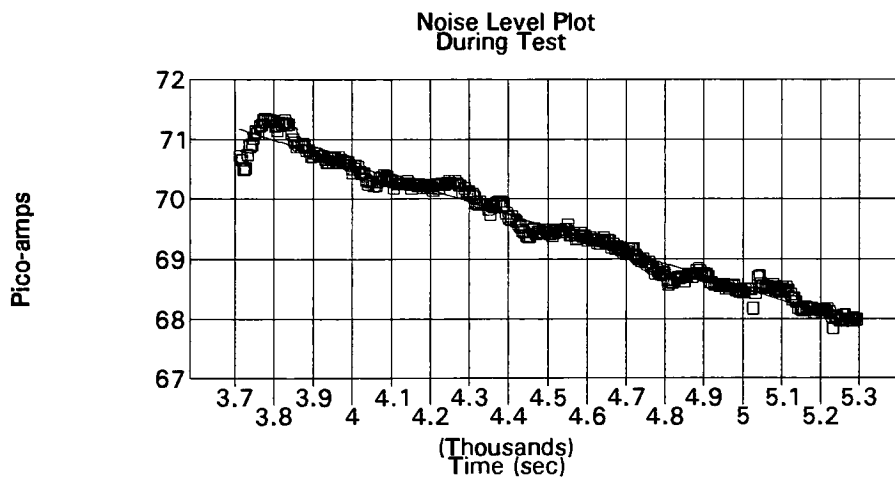
3495 time 3675 5294  
amps 70.02

f1:range f2:remove f3:adjust f4:slope f5:subtract f6:prn file f7:exit

DATA FILE:	0525AOHA	UPPER LIMITS
FILM:	AOH	
PERMEANT:	Linalool	

93

Noise	0.977022 Pico-amps
Test Time	1581.64 sec



Diffusion < =	2.276118 (1/hrs)
Permeation < =	0.262998 microgram/m <sup>2</sup> .hr

NOTES: High noise due to not enough equilization time between calibration and test. More time needed in test mode.

FIGURE 25

Data File: 0526A0HE

Calibration File: 0524BxA

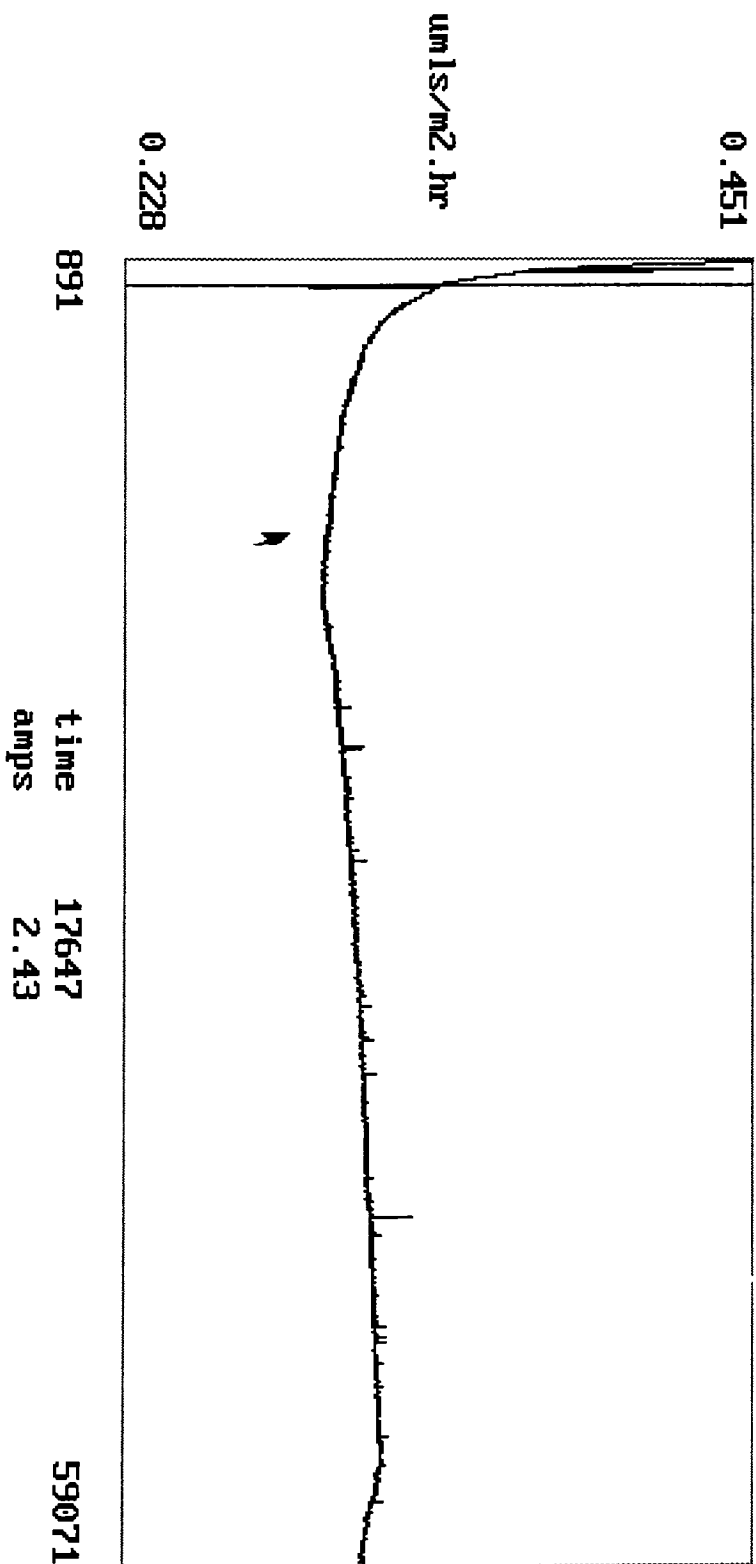
material: AOH  
caliper: .84permeant: Black Tea  
concentration: 1  
vapor pressure: .314  
injection: .25cell temp: 100  
fid temp: 150

FIGURE 26

f1:range f2:remove f3:adjust f4:slope f5:subtract f6:prn file f7:exit



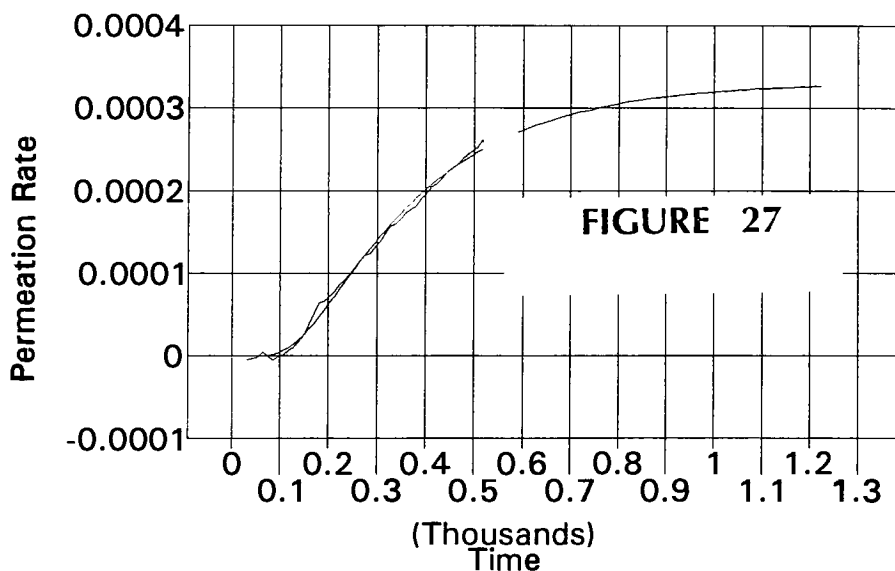
File: **0526AOHE**  
 Date: **05-27-94**  
 Time: **10:09:09**

Material: **AOH**  
 Caliper (mils): **0.84**

Permeant: **Black Tea**  
 PPM V **Unknown**

Temperature (deg c): **100**

Permeation Data  
Actual and Projected



Time Units:

*minutes*

Permeation Rate Units:

*u/mls/m2.hour*

#### Parameter Estimates

Baseline (pico amperes):

Steady State Permeation:

Diffusion (1/hours):

Value	Std. Error	% error
<b>2.537339</b>	<b>0.002820</b>	<b>0.111146</b>
<b>0.000331</b>	<b>0.002018</b>	<b>609.4760</b>
<b>0.024630</b>	<b>0.001615</b>	<b>6.557069</b>

Half Life:

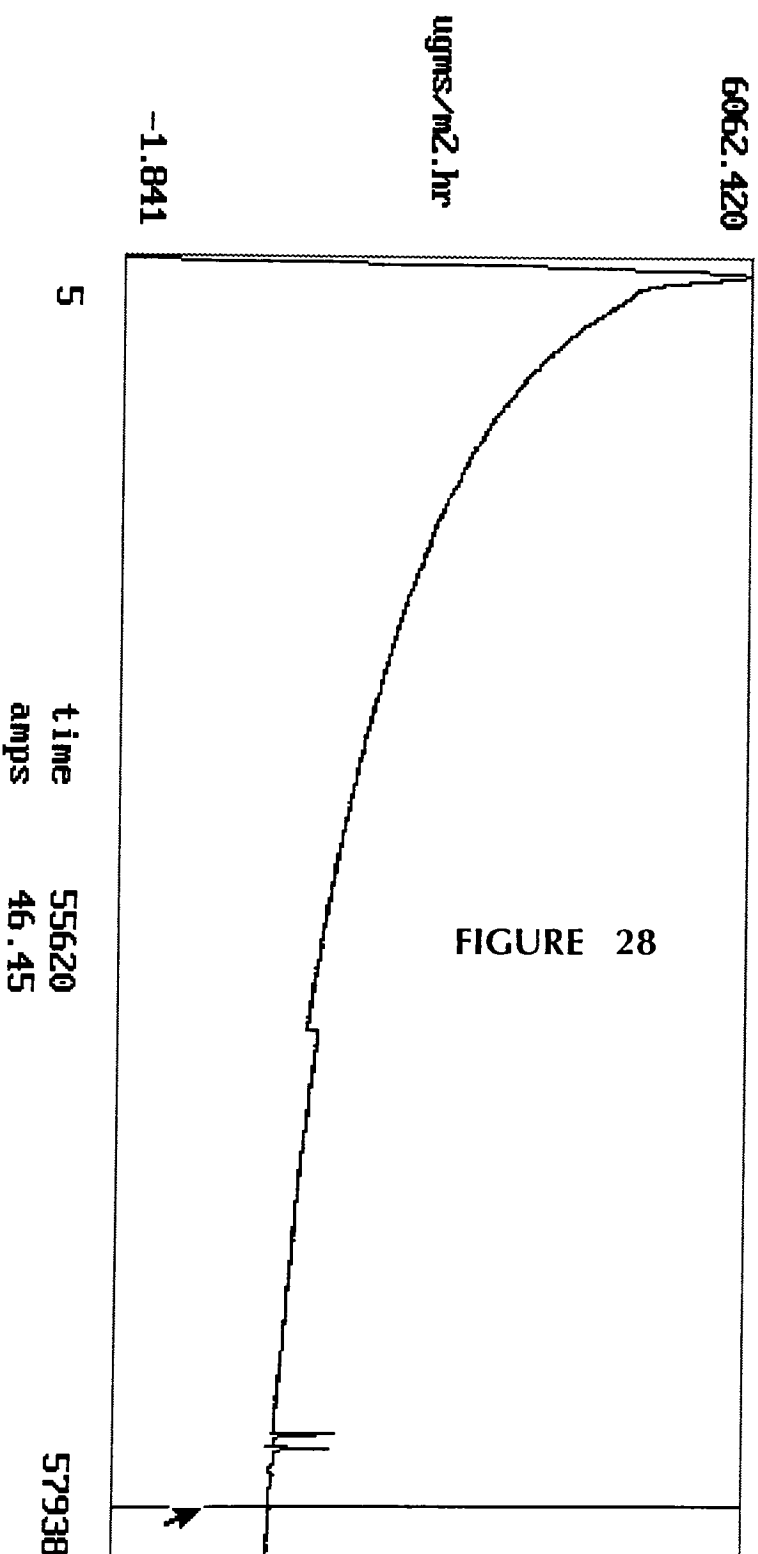
**337.7710 minutes**

#### Material Coefficients

Permeation	0.000278 u/mls.mil/m2.hour
Diffusion	0.017379 mil.mil/hour
Solubility	0.016008 u/mls/mil.m2

Data File: 0524BXA

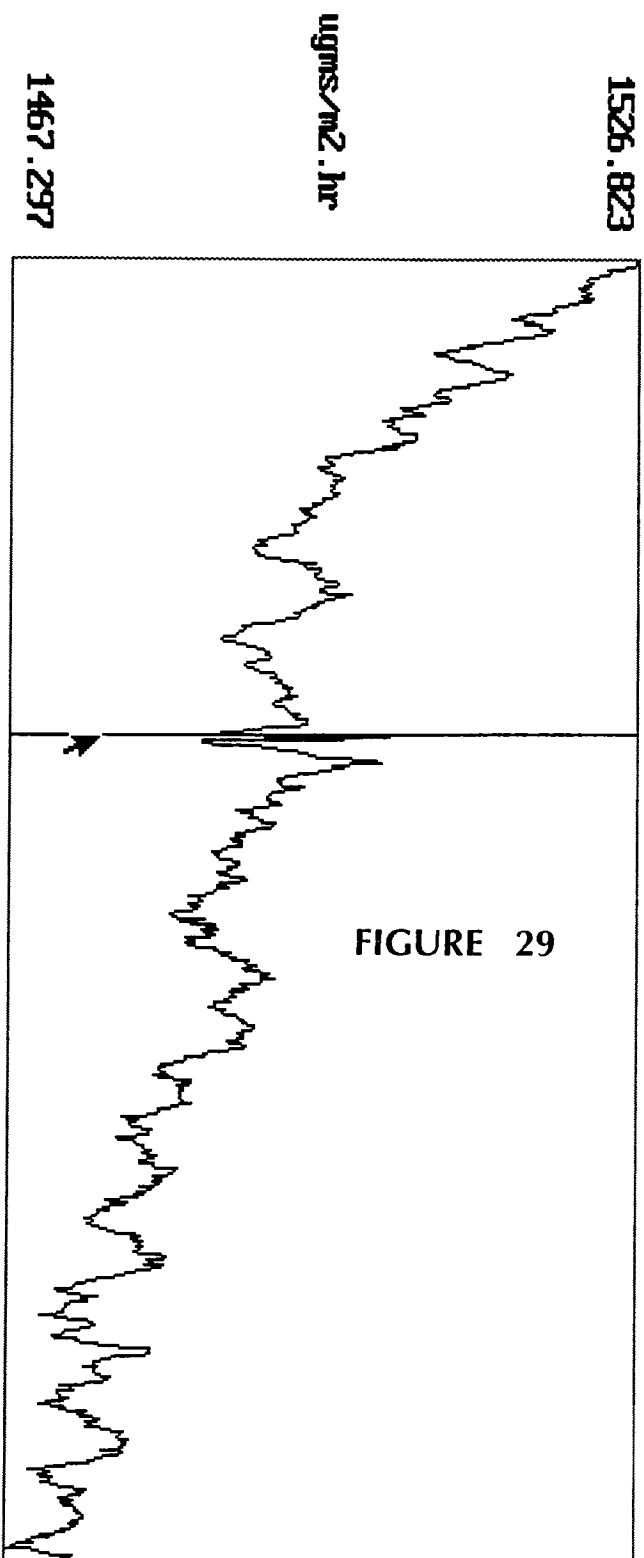
Calibration File: 0524BXA

material: BX25  
caliper: 1permeant: Linalool  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 150

f1:file f2:edit f3:analysis f4:exit

Data File: 0524BXA

Calibration File: 0524BXA

material: BX25  
caliper: 1permeant: Linalool  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 150

54313

55632  
79.96

57938

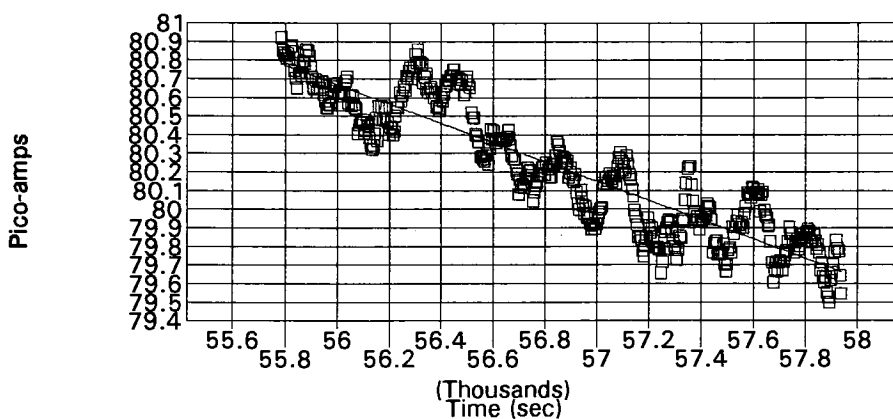
f1:range f2:remove f3:adjust f4:slope f5:subtract f6:prn file f7:exit

DATA FILE:	0524BXA	UPPER LIMITS
FILM:	Barex	
PERMEANT:	Linalool	

98

Noise	0.832720 Pico-amps
Test Time	2152.64 sec

Noise Level Plot



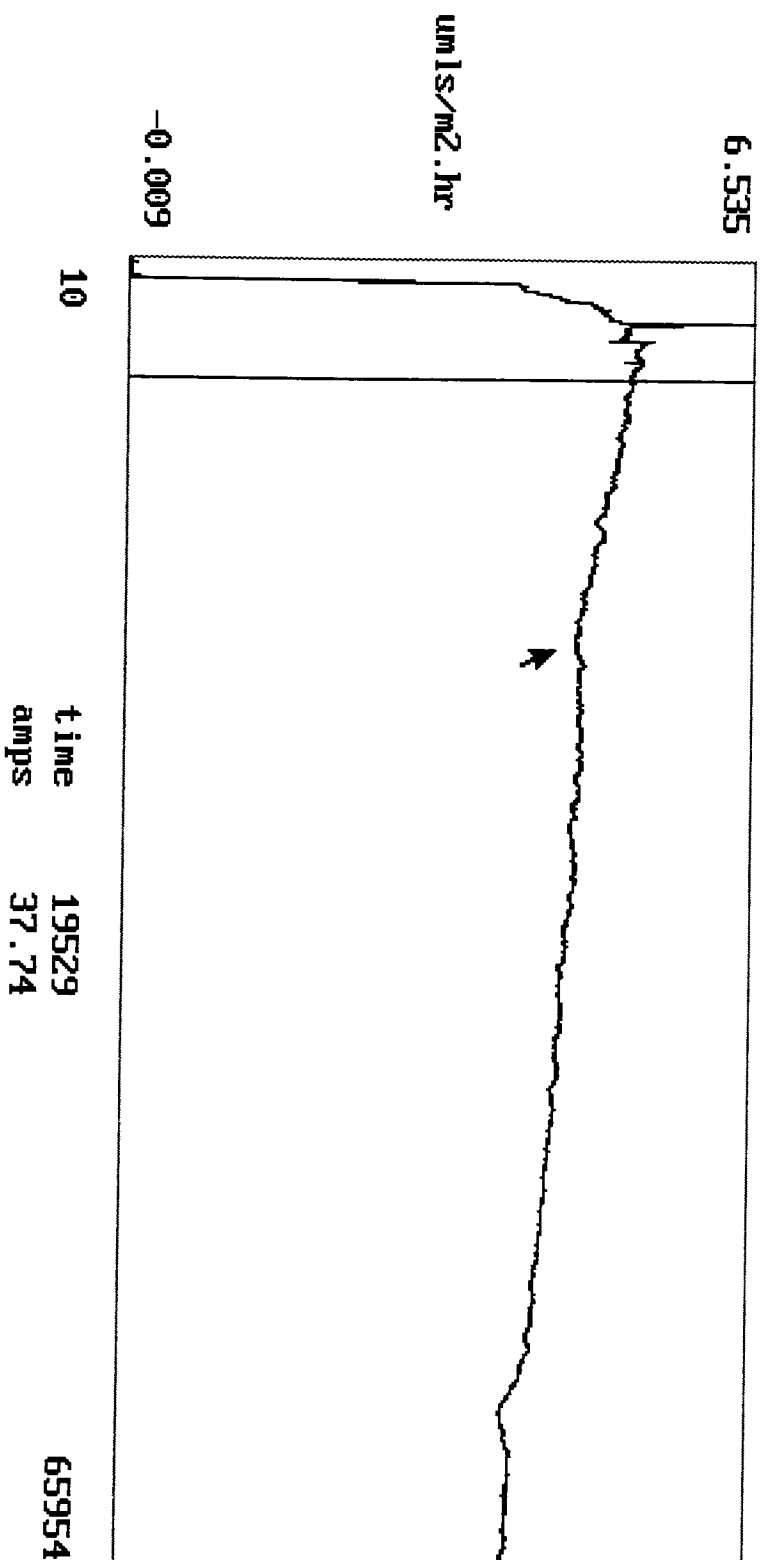
Diffusion < =	1.672365 (1/hrs)
Permeation < =	0.224155 microgram/m2.hr

NOTES: High noise can be attributed to temperature fluxuations occuring at a cell temp of 100 deg C. Test time should have gone longer.

FIGURE 30

Data File: 0526BXD

Calibration File: 0524BXA

material: Barex  
caliper: 1permeant: BLACK TEA  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 150

f1:range f2:remove f3:adjust f4:slope f5:subtract f6:prn file f7:exit

FIGURE 31

Data File: 0526BXD

Calibration File: 0524BXA

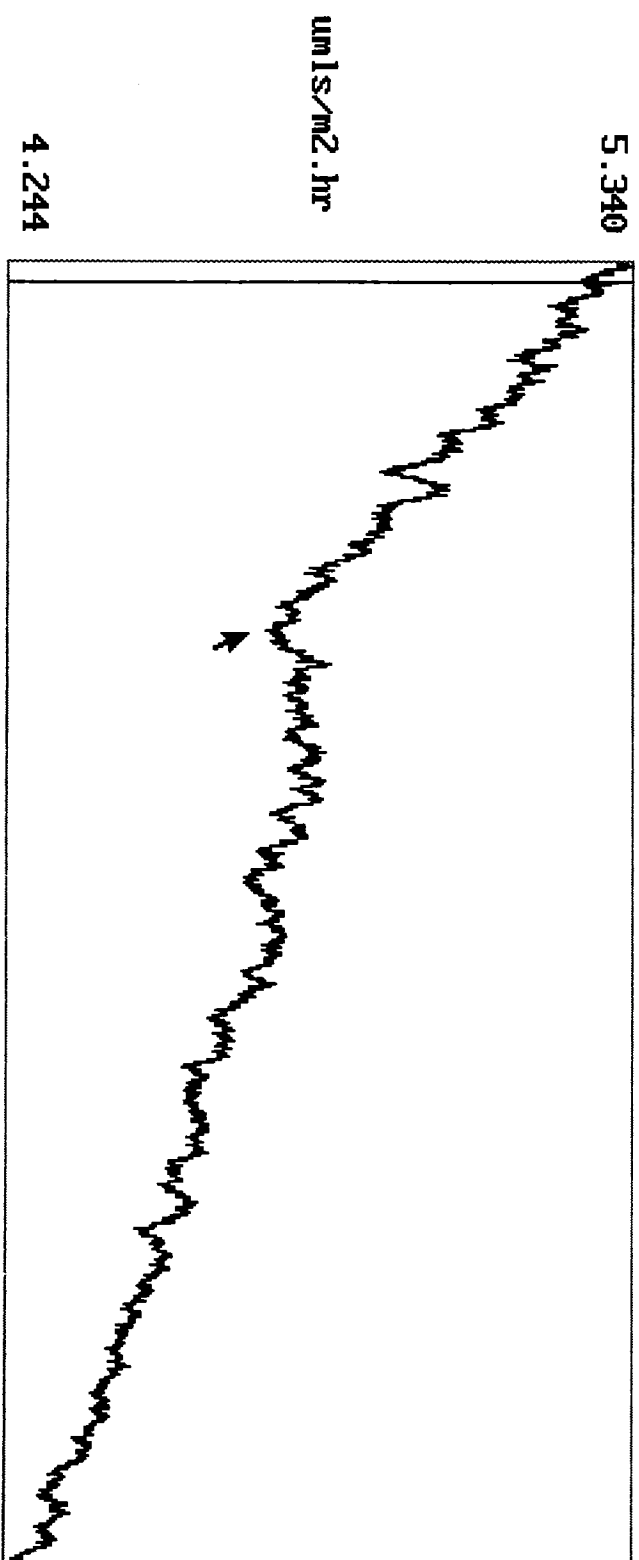
material: Barex  
caliper: 1permeant: BLACK TEA  
concentration: 1  
vapor pressure: .313  
injection: .25cell temp: 100  
fid temp: 150

FIGURE 32

f1:range f2:remove f3:adjust f4:slope f5:subtract f6:prn file f7:exit

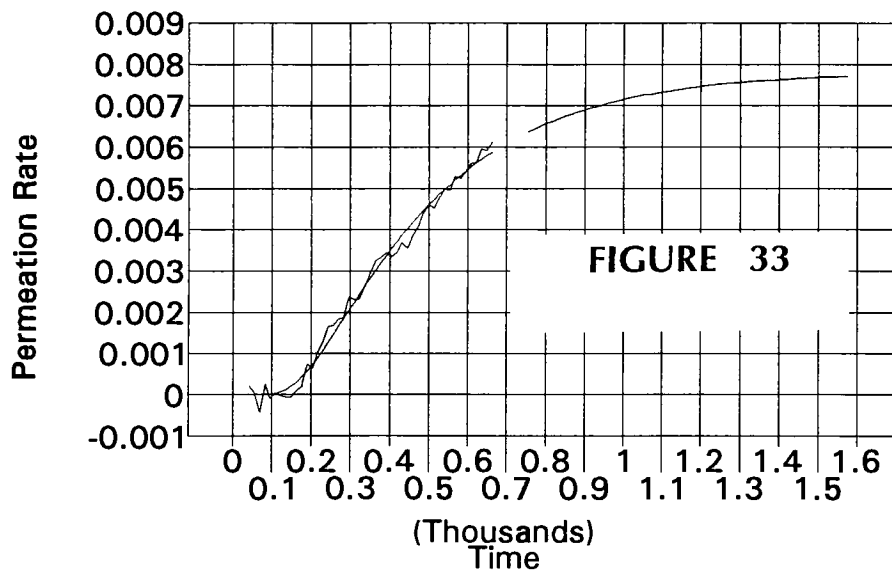
File:	<b>0526BXD</b>
Date:	<b>05-27-94</b>
Time:	<b>09:52:44</b>

Material:	<b>Barex</b>
Caliper (mils):	<b>1</b>

Permeant:	<b>BLACK TEA</b>
PPM V	<b>Unknown</b>

Temperature (deg c):	<b>100</b>
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Permeation Data  
Actual and Projected



Time Units: **minutes**  
Permeation Rate Units: **u/mls/m<sup>2</sup>.hour**

Parameter Estimates  
Baseline (pico amperes):  
Steady State Permeation:  
Diffusion (1/hours):

Value	Std. Error	% error
<b>43.27891</b>	<b>0.092120</b>	<b>0.212853</b>
<b>0.007827</b>	<b>0.067894</b>	<b>867.4273</b>
<b>0.019085</b>	<b>0.001768</b>	<b>9.267666</b>

Half Life: **435.9089 minutes**

Material Coefficients

Permeation	<b>0.007827 u/mls.mil/m<sup>2</sup>.hour</b>
Diffusion	<b>0.019085 mil.mil/hour</b>
Solubility	<b>0.410111 u/mls/mil.m<sup>2</sup></b>